COMPARATIVE STUDY OF ALTERNATIVE FUEL ICING INHIBITOR ADDITIVE

PROPERTIES & CHEMICAL ANALYSIS OF METAL SPECIATION IN AVIATION

FUELS

Thesis

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An investigation was conducted to compare some important properties of the current fuel system icing inhibitor, Diethylene Glycol Monomethyl Ether (DiEGME), with a candidate replacement additive, Triethylene Glycol Monomethyl Ether (TriEGME), and their solutions with fuel or water. The results indicate that TriEGME has similar solution properties and chemical behavior to DiEGME in evaluation of dissolution rate, freeze point suppression, viscosity, water solubility, and fuel/water partitioning. These results, combined with other independent evaluations, show that TriEGME has the necessary properties for replacement of DiEGME as a fuel system icing inhibitor additive. A principal benefit to the use of TriEGME is due to its relatively low volatility, which prevents degradation of topcoat material in fuel tank ullage areas. An analytical method was developed for the quantification and characterization of copper speciation in jet fuels using High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS) with electrospray ionization. The method was used to successfully detect and quantify low levels of N,N?-disalicylidene-1,2-propanediamine (MDA) and the complex formed between MDA and Cu(II) ions. The results indicate that HPLC-MS with electrospray ionization should be generally applicable for the detection and quantification of metal complexes in hydrocarbon solutions. The identification of metal complexes in fuels should greatly increase the understanding of the fundamental reaction processes which cause fuel degradation during storage and use.

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ABSTRACT

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ACKNOWLEDGEMENTS

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LIST OF SYMBOLS AND ABBREVIATIONS

FSII	Fuel System Icing Inhibitors
EGME	Ethylene Glycol Monomethyl Ether
DiEGME	Diethylene Glycol Monomethyl Ether
B-52	Boeing B-52 Stratofortress
FTTP	Fuel Tank Topcoat Peeling
TriEGME	Triethylene Glycol Monomethyl Ether
mmHg	millimeters of mercury
JP	Jet Propellant
RH	hydrocarbons
O_2	dissolved oxygen
SH	hydroperoxide decomposers
ROOH	hydroperoxides
$AH\bullet$	peroxy radical inhibitors or antioxidants
$A\bullet$	antioxidant radical
A	Arrhenius parameters (mol, L, s)
MDA	N,N'-disalicylidiene-1,2-propanediamine
MDA	Metal Deactivating Additive
g	grams

mol	mole
3-D	three dimensional
FAAS	Flame Atomic Absorption Spectroscopy
KCF_3SO_3	Potassium Trifluoromethanesulfonate
μg	microgram
UV	Ultra Violet
PVA	poly(vinyl alcohol)
AA	Atomic Absorption
HPLC-MS	High Performance Liquid Chromatograhy Mass Spectrometry
HPLC-AA	High Performance Liquid Chromatograph Atomic Absorption
EPA	US Environmental Protection Agency
NIOSH	National Institute for Occupational Safety and Health
AOAC	Association of Official Agricultural Chemists
APHA	American Public Health Association
Cu(II)AcAc	Copper(II)Acetoacetonate
Jet A-1	aviation fuel
MDA-Cu(II)	N,N'-disalicylidiene-1,2-propanediamine-copper
ESI	Electrospray Ionization
APCI	Atmospheric Pressure Chemical Ionization Interfaces
GC	Gas Chromatography
ASTM	American Society for Testing and Materials
AFRL	Air Force Research Laboratory
UDRI	University of Dayton Research Institute

WPAFB	Wright Patterson Air Force Base (OH)
SALEMS	Sub-Ambient Liquid Equilibrium Measurement System
MS TOF	Mass Spectrometry Time of Flight
LC	Liquid Chromatography
DSC	Differential Scanning Calorimetry
vol %	percent by volume
ppm	parts per million
ppb	parts per billion
m/z	mass to charge ratio
$\pm$	plus or minus
$\leq$	greater or less than

CHAPTER I

INTRODUCTION

Research Areas:

Two areas of study were addressed in this manuscript; the first being the

properties of TriEGME compared to DiEGME in regards to fuel icing inhibitor additive

replacement; the other being a study of metal speciation chemistry of copper using N,N'-

disalicylidene-1,2-propanediamine (MDA).

Fuel System Icing Inhibitor Additives:

Petroleum is composed of a diverse mixture of hydrocarbons such as paraffins,

olefins, cyclo-parafins (naphthenes), aromatics and a host of trace species. Petroleum

distillates such as jet fuels are also a complex mixture of hydrocarbons. The crude source

of these mixtures, and refinery processes used, play a major role in their

physical/chemical identity and properties such as energy content, combustion

characteristics, density, fluidity, lubricity, stability, corrosivity and electrical

conductivity. The ability to characterize these components along with the many additives

used to complement them is of major concern for the United States military (Striebich et

al., 2000).

Jet fuel, used by the United States military, plays a vital role in safety and security

of the nation's people and interests. It is no surprise that extensive investments in time

and money have been applied to discover new technologies and applications for the better use of these fuels. Jet fuel additives offer a wide range of properties that fuels and mechanical components themselves could not feasibly offer, such as but not limited to icing inhibition, corrosion protection, static dissipation, and thermal stability.

Fuel system icing inhibitors (FSII) are incorporated into military jet fuels to prevent ice crystal formation in the fuel and/or fuel systems which could plug filters and fuel lines during high altitude flights in which the outside air temperatures can be below -70°C. As result of the unfortunate crash of a B52- Stratofortress in 1959 which was attributed to ice blockage of fuel lines, icing inhibitor additives became required in fuels for military operation in 1961. The history of icing inhibitor additives for jet fuel begins with Ethylene Glycol Monomethyl Ether (EGME) which due to toxicity and volatility issues was subsequently replaced with Diethylene Glycol Monomethyl Ether (DiEGME) in 1992 (Martel, 1987). DiEGME is currently the only approved icing inhibitor additive for JP-5 and JP-8 fuels with a specified procurement concentration of 0.10-0.15 vol % and a minimum use concentration of 0.03 vol % for JP-5 and 0.07 vol % for JP-8 fuels. Figure 1 depicts the chemical line structures of EGME and DiEGME.
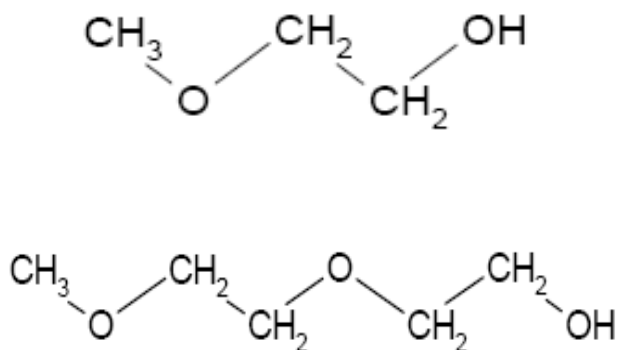
Figure 1. Structures of Ethylene Glycol Monomethyl Ether (EGME) and DiEthylene Glycol Monomethyl Ether (DiEGME)

Fuel Tank Topcoat Failure:

Some problems have arisen with the use of DiEGME as the principal icing inhibitor agent over the past two decades. B-52 aircraft fuel tanks have experienced fuel tank topcoat failure in which the topcoat material begins to swell and peel due to absorption of DiEGME (Aliband et al., 2006). Glycol ethers have long been used as paint strippers, but surprisingly, at concentrations less than 0.1 vol %, this phenomena still takes place and has become a major concern of the United States military (Aliband et al., 2006). Figure 2 shows FTTP occurring for B-52 fuel tank topcoat panels and Figure 3 illustrates the absorption phenomena. DiEGME, which is more volatile than most fuel components, concentrates in the vapor phase, condenses on the cold fuel tank walls and is subsequently absorbed into the topcoat paint. The absorption results in topcoat deterioration where adhesion to the metal surface is lost creating flakes which can plug fuel filters and valves.

Figure 2. Fuel tank topcoat peeling (FTTP) occurring in B-52 wing tank test panels (Aliband et al., 2006)
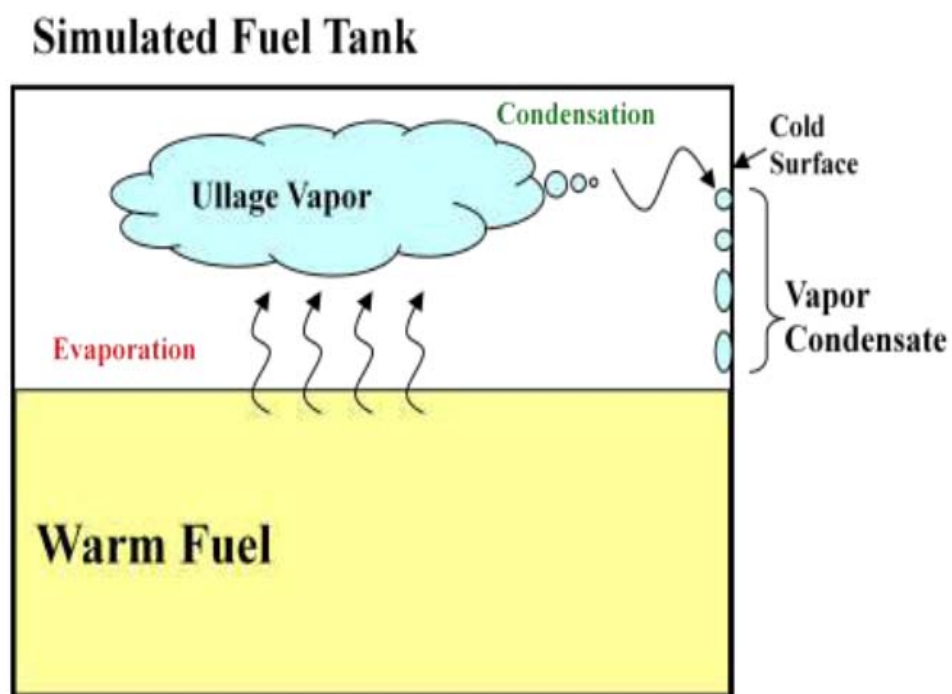
Figure 3. FTTP absorption phenomena onto topcoat protected fuel tanks due to DiEGME

Triethylene Glycol Monomethyl Ether (TriEGME) has been proposed to supplant

DiEGME as the specified required fuel icing inhibitor additive (Zabarnick et al., 2007)

TriEGME, in theory, should have the same icing inhibiting abilities as DiEGME, due to

their similar chemical structure and polarity and should not cause FTTP due to its

significantly lower vapor pressure. TriEGME has a vapor pressure of <0.01 mmHg at

$20^{o}C$ which is an order of magnitude lower than DiEGME at 0.19 mmHg at $20^{o}C$

(Zabarnick et al., 2007). Figure 4 depicts the chemical line structure of Triethylene

Glycol Monomethyl Ether.
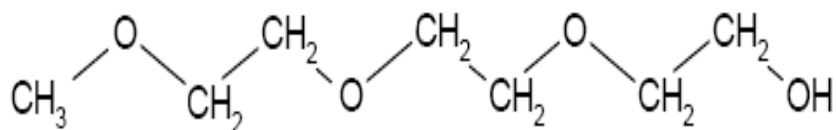
Figure 4. Structure of Triethylene Glycol Monomethyl Ether (TriEGME)

Replacement of DiEGME:

Replacing DiEGME with TriEGME will require an in depth analysis of the

changes in fuel/fuel system component compatibility. Table 1 shows some of the

property differences between DiEGME and TriEGME (Zabarnick et al., 2007). Extensive

studies have already been performed in regards to FTTP, and TriEGME has proved to

have great potential in ultimately replacing DiEGME in the long run. In the current work,

we explore the effect of a proposed transition to the use of TriEGME on fuels and fuel

system operation. The experiments in this study were focused on comparing the

properties of TriEGME and DiEGME, and their solutions with fuel and water, such as

dissolution rate, freeze point suppression, viscosity, water solubility, and temperature

dependent fuel/water partitioning. The analysis of these results will help determine if

TriEGME is a feasible option for the replacement of DiEGME in the long run.

Table 1. Properties of DiEGME and TriEGME

FSII Additive	Vapor Pressure (mmHg @ 20°C)	Density (g/mol @ 20°C)	Molecular Weight (g/mol)	Freeze Point (^{o}C)
DiEGME	0.19	1.023	120	-85
TriEGME	< 0.01	1.026	164	-47

Jet Fuel Thermal Stability and Metal Catalyzed Autoxidation:

Jet fuels are a mixture of diverse hydrocarbon chemical species that serve as a fuel source for jet aircraft engines. Jet fuels also contain trace amounts of metal ions such as copper, iron, and zinc which may have strong pro-oxidant capabilities (Pederson et al., 1939). The oxidation of fuel consists of a mechanism of chemical chain propagation and branching reactions where fuels deteriorate, resulting in fouling of surfaces and plugging of nozzles and valves. The basic autoxidation mechanism is shown in Figure 5 which shows the most important reactions in determining fuel oxidation behavior.
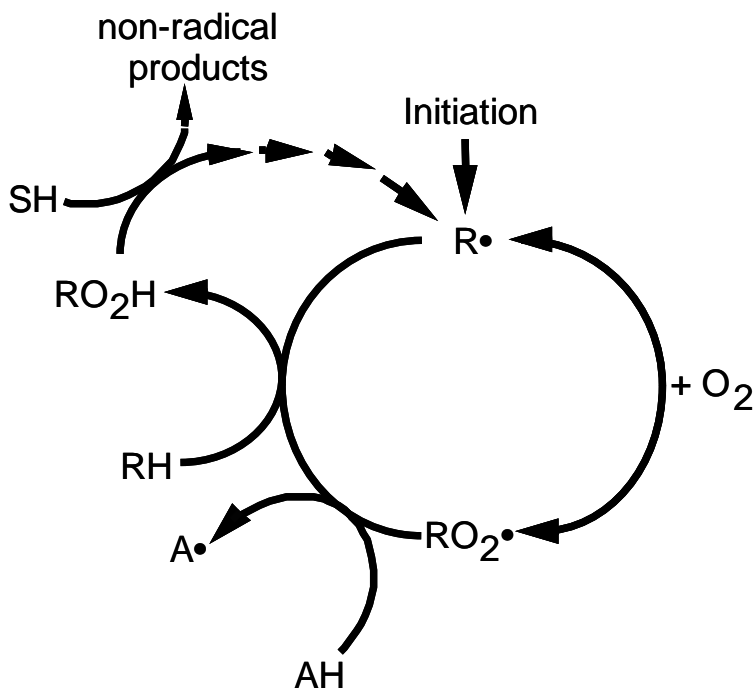
Figure 5. Diagram of the autoxidation reaction process (Zabarnick et al., 2007)

The species classes shown in the autoxidation mechanism are: hydrocarbons (RH), dissolved oxygen (O_2), peroxy radical inhibitors or antioxidants (AH), hydroperoxide decomposers (SH), and hydroperoxides (ROOH). Metals serve as a catalyst to these autoxidative chain reactions where the production of free radicals causes the deterioration of fuels. The chemical kinetic mechanism and associated Arrhenius parameters portraying the basic autoxidation cycle is shown in Table 2.

Table 2. Chemical Kinetic Mechanism of Fuel Oxidation (Kuprowicz et al., 2007)

#	Reaction	A (mol, L, s)	E_a (kcal/mol)
1	$I \rightarrow R\bullet$	1×10^{-3}	0
2	$R\bullet + O_2 \rightarrow RO_2\bullet$	3×10^9	0
3	$RO_2\bullet + RH \rightarrow RO_2H + R\bullet$	3×10^9	12
4	$RO_2\bullet + RO_2\bullet \rightarrow$ termination	3×10^9	0
5	$RO_2\bullet + AH \rightarrow RO_2H + A\bullet$	3×10^9	5
6	$A\bullet + RH \rightarrow AH + R\bullet$	1×10^5	12
7	$A\bullet + RO_2\bullet \rightarrow$ Products$_{AH}$	3×10^9	0
8	$R\bullet + R\bullet \rightarrow R_2$	3×10^9	0
9	$RO_2H \rightarrow RO\bullet + \bullet OH$	1×10^{15}	39
10	$RO\bullet + RH \rightarrow ROH + R\bullet$	3×10^9	10
11	$RO\bullet \rightarrow R_{prime}\bullet +$ carbonyl	1×10^{16}	15
12	$\bullet OH + RH \rightarrow H_2O + R\bullet$	3×10^9	10
13	$RO\bullet + RO\bullet \rightarrow RO\bullet_{term}$	3×10^9	0
14	$R_{prime}\bullet + RH \rightarrow$ alkane $+ R\bullet$	3×10^9	10
15	$RO_2H + SH \rightarrow$ Products$_{SH}$	3×10^9	18
16	$RO_2\bullet \rightarrow R\bullet + O_2$	1×10^{16}	19
17	$RO_2\bullet + R\bullet \rightarrow$ termination	3×10^9	0
18	$RO_2H + M \rightarrow RO\bullet + \bullet OH + M$	3×10^{10}	15

Jet Fuel Thermal Stability Additive MDA & Metal Speciation:

N,N'-disalicylidene-1,2-propanediamine (MDA) shown in Figure 6 is a metal deactivating additive that has been used for over seven decades in order to inhibit metal catalyzed fuel oxidation reactions for improved fuel thermal and storage stability. At a molecular weight of 282.34 g/mol, MDA contains two amine and hydroxyl groups. Due to these two functional groups present on the compound, MDA interacts very strongly with metal ions and has been shown to effectively eliminate autocatalysis due to their presence in fuel mixtures (Striebich et al., 2000). Figure 6 shows the 3-D theoretical form that MDA would have in a fuel solution.
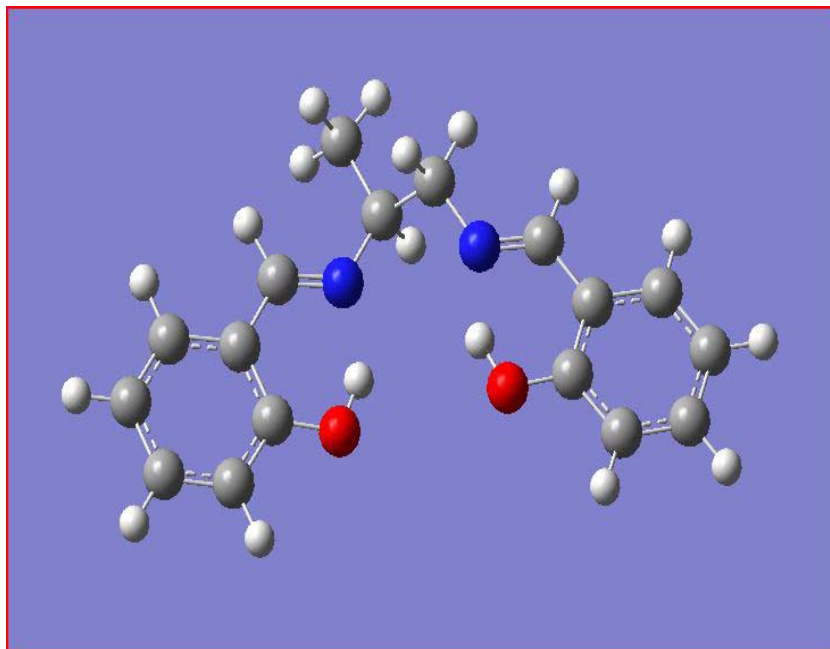
Figure 6. 3-D structure of MDA

The spheres shown in the above diagram of MDA are: grey (carbons), white (hydrogens), red (oxygens) and blue (nitrogens) with single and double bonds represented by one and two white lines respectively. The strong interaction of MDA with ions has

made development of analysis techniques challenging as extreme care must be taken due to its ability to absorb onto surfaces such as glassware, filters, sample vials and syringes (Striebich et al., 2000). Derivatization techniques, such as silylation, have been developed to reduce the interactive properties of MDA, greatly increasing the ability to quantitatively transfer and analyze the species (Striebich et al., 2000). In the fuel environment with the presence of many potential metal ion binding partners, MDA can exist in a number of distinct complexes. Unfortunately, these complexed forms of MDA have rarely been shown to be amenable to chemical analysis (Taylor and Synovec, 1994). Also, the identity and forms of metal complexes in fuel are poorly understood.

Researchers in a number of different disciplines seek to understand the speciation of metals in solution. Specifically, the development of methods capable of identifying the speciation of metals in solution is desired where information such as catalytic activity, transport mechanisms, bioavailability, and mobility of metals in systems can be understood (Taylor and Synovec, 1994). For military jet fuels, metal speciation is important for understanding the chemistries of metal associated thermal stability. Figure 7 shows the 3-D theoretical form that a MDA-Cu(II) complex would exist in a fuel solution after the reaction between MDA and a copper source. The spheres shown in the diagram of MDA-Cu(II) complex below are: grey (carbons), white (hydrogens), red (oxygens), blue (nitrogens) and gold (copper 2^+) with single and double bonds represented by one and two white lines, respectively.
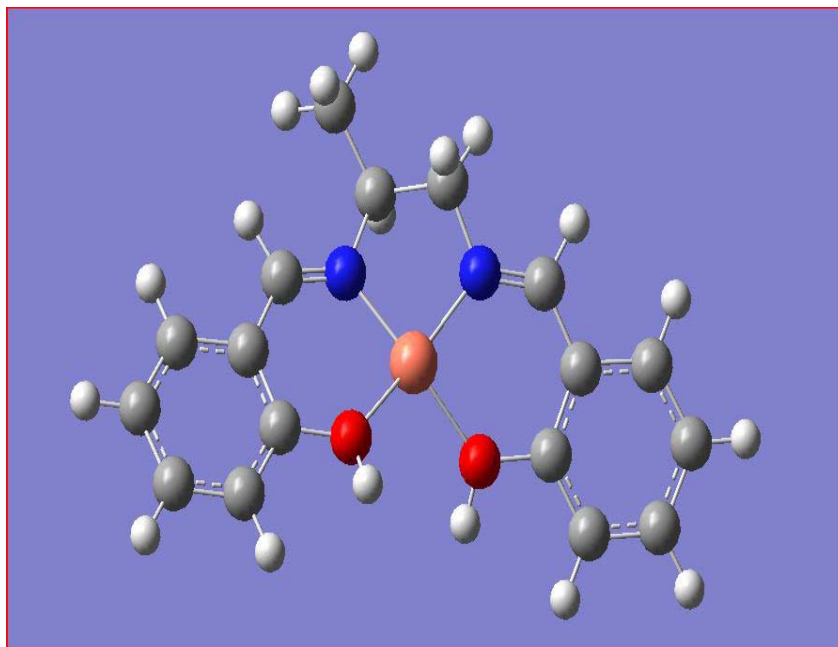
Figure 7. 3-D structure of MDA-Cu(II) complex

Method Development to Characterize Metal Speciation:

A method able to determine the speciation of metals in a fuel matrix will

eventually lead to a greater understanding of the interactions involving those metals than

current methods are able to accomplish. Until recent years, the ability to understand metal

chemistry has been limited to the determination of bulk concentration of those metals in

solution (Taylor and Synovec, 1994). A pilot method in identifying metal speciation in a

fuel matrix was developed by Taylor and Synovec at the University of Washington in

1994 using the High Performance Liquid Chromatography and Atomic-Absorption

(HLPC-AA) instrument. This method involved using a dual normal-phase/ion-exchange

mechanism where the separation of three different copper complex compounds; copper

cyclohexanebutryrate, copper tetramethylheptanedionate and N,N'-disalicylidene-1,2-

propylenediaminocopper were achieved. A polymeric stationary phase poly(vinyl

alcohol) or PVA using a ternary gradient of 2-propanol, acetonitrile, and 10mM

KCF_3SO_3 in methanol was used to achieve separation of the standard copper compounds

aforementioned. The gradient system solvent program in conjunction with Flame Atomic

Absorption Spectroscopy (FAAS) detection allowed for each copper complex to be

successfully separated and quantified with a detection limit of 10 µg/L. This method

provided a valuable tool in determining the copper species responsible for catalytic

autoxidation and degradation of aerospace fuels. These results paved the way for further

experimentation using the HPLC-MS instrument for determination and characterization

of MDA and copper speciation at even lower detection limits. The advantage of using

HLPC-MS compared to HPLC-AA is that mass spectrometry allows the ability to

identify unknowns without the need for chromatographic separation while atomic

absorption (AA) is simply an analytical technique for determining the concentration of a particular metal element within a sample. The optical system used for AA analysis must also be specifically set to characterize the particular metal element of interest which does not allow for easy analysis of unknowns.

High Performance Liquid Chromatography & Mass Spectrometry:

HPLC-MS is an analytical chemistry technique that couples the physical separation capabilities of liquid chromatography with the mass analysis capabilities of mass spectrometry. This highly sensitive technique is oriented toward the specific detection and potential identification of chemicals in a complex mixture. HPLC-MS consists of a High Performance Liquid Chromatogram connected to a Mass Spectrometer. This type of instrumental linkage for chemical analysis is termed a "hyphenated method" for its chromatographic and spectral methods (Gates, 2008). Solutions prepared for analysis are injected into the HPLC column made of stainless steel tubing usually 150 mm length and 2-20 mm internal diameter packed with very small, chemically modified silica particles. The sample compounds are then separated on the basis of their relative interaction with the chemical coating of these compounds termed the stationary phase and the solvent flow through the column termed the mobile phase. The components that elute from the column are escorted to the mass spectrometer via a specialized interface. The two most common interfaces used in HPLC-MS are the electrospray ionization (ESI) and the atmospheric pressure chemical ionization interfaces (APCI). The purpose of the electrospray ionization technique is to produce ions and is especially useful in producing ions from macromolecules because it overcomes the propensity of these molecules to fragment when ionized (Gates, 2008). The electrospray ionization technique was developed by Nobel Prize chemist John Bennett Fenn and was originally designed for biological macromolecules but is also used for other types of compounds (e.g. petroleum distillates) (Fenn and Yamashita, 1984). Electrospray ionization consists of the sample being introduced to the ion source at micro-liter per minute flow rates. The flow of

solution passes through an electrospray needle that has a high potential difference applied to it. This potential difference forces the spraying of charged droplets from the needle with a surface charge of the same polarity to the charge of the needle. The droplets are then propelled from the needle toward a source sampling cone on a counter electrode. The droplets traverse the space between the needle tip and cone in which the solvent is evaporated. As the solvent is evaporated, the droplet progressively shrinks until it reaches a point of critical surface tension where it can no longer sustain its charge (Fenn et al., 1989). This limit is termed the "Rayleigh Limit" and when it has been exceeded, a "Coulombic Explosion" occurs in which the droplet is ripped apart and smaller droplets disperse (Gates, 2008). The process is then repeated for the smaller dispersed droplets, along with the naked charged sample molecules that were embedded in the solvent. These sample molecules or "analytes" come in the form of singly charged or multiple charged species. In regards to petroleum analysis, the major hurdle is getting the analyte within the hydrocarbon matrix to ionize consistently for analysis. Below, is a scheme of the mechanism of ion formation illustrated by Dr. Paul Gates at the University of Bristol in the United Kingdom.
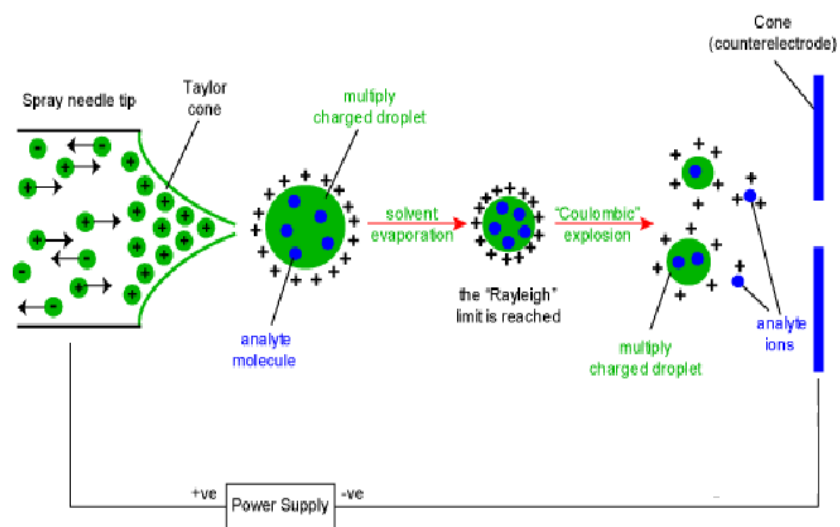
Figure 8. Mechanism of ion formation (P. Gates 2008)

Experimental Goals:

Investigative studies of TriEGME and DiEGME fuel solubility, freeze point, aqueous phase partitioning, viscosity, and surface tension were performed. These studies were conducted in order to deternine if TriEGME could serve as a feasible, long term replacement of DiEGME as the primary fuel icing inhibitor additive for JP-8 fuel.

A method designed for the determination of concentrations of metal compounds present in fuels along with the speciation of those metals is desired. Such a method would not only help researchers determine the identity of the metal, but the form it takes when metal complexes are formed. Studies were performed to quantitatively calibrate and qualitatively characterize MDA, Cu(II)AcAc , and the MDA-Cu(II) complex in solution using the HPLC-MS instrument. Concentration standards for the studied compounds were tested in methanol and 5237 Jet A-1 fuel. These studies will provide insight into the form and reactivity of metal ions in jet fuel solutions.

CHAPTER II

EXPERIMENTAL

Equilibrium Dissolution Studies

Experiments were conducted to determine the equilibrium solubility of FSII in

5237 Jet A-1 fuel solutions with respect to time and temperature. The solubility

characteristics of DiEGME and TriEGME in aviation fuel under moderately stirred

conditions via a magnetic stir bar for a duration of 1-60 mins were determined. The

testing rig consists of a 500 mL tinted glass bottle, syringe, magnetic stir bar and plate,

and a glass jacketed vessel. Preparing 325.5 mL of standard solution of 5237 Jet A-1 into

a tinted glass jar surrounded by a Kontes Scientific jacketed vessel, attached to a Thermo-

NESLAB ULT 950 chiller, these solutions were brought to the desired testing

temperature range between -47 to 20°C. Temperature readings were taken with a type-K

thermocouple attached to an Omega HHM31 thermocouple reader. 24.5 mL of DiEGME

and or TriEGME were slowly added to the solution at temperature to reach an overall

concentration of 7 vol % FSII in fuel

Using a 10 mL syringe, 2 mL samples of the solution were taken and analyzed using a Agilent Technologies 7890A/5975C GC System MSD to determine the concentration of FSII in fuel. The GC column was a 30-meter DB-5MS capillary column (0.25mm ID and 0.25μm film). The GC temperature program employed an initial temperature of 40°C (0.5-minute hold) followed by ramping (10°C/min) to 200°C and then 30°C/min to 290°C (10-minute hold). A constant column flow rate of 1 mL/min, and 20:1 split 1-μL injections were used. The GC injector temperature was 275°C, and the Agilent Model 5975 mass spectrometer transfer line was held at a temperature of 280°C. Before GC analysis, each sample was diluted within a range of (1:10, 1:20, 1:50, 1:100) with hexanes as the solvent. An internal standard (tetracosane – $C_{24}H_{50}$) was also used and prepared in DiEGME or TriEGME-free fuel diluted at the same ratio in hexanes as the samples and analyzed.

Differential Scanning Calorimetry (DSC) Study

Standard solutions of FSII/water ranging from 0-50% of FSII by volume were prepared in 10% intervals. During testing, approximately 20 mg of liquid sample were injected using a 50 mL syringe into an aluminum pan and used for analysis. Samples were measured using a Sartorius AC 1215 Max 120 gram mass balance linearity calibrated with accuracy $\pm$ 0.0005 g. The DSC temperature program used for the analysis of DiEGME was a cooling rate of 1^oC/min to -70^oC, followed by heating at 0.25^oC/min and for TriEGME a cooling rate of 1^oC/min to -85^oC, followed by heating at 0.5^oC/min. Mixtures above 50 volume percent were sent to another lab and tested using the ASTM D1177 method.

Aqueous Viscosity Studies

Experimentation was conducted using a Tannas Scanning Brookfield Plus Two Viscometer at sub-ambient temperatures ($< 20^o$C). This instrument has been used within AFRL/RZTG's JP-8+100LT program to provide insight into the effect of temperature on the flow characteristics of hydrocarbon-based fuels in addition to the evaluation of additives designed to suppress the onset of solidification. For each concentration of TriEGME, the viscometer was set to have a rotor speed of 12 RPM and a temperature ramp rate of -2°C/hr from an initial temperature of 20^oC. Viscosity measurements were made for aqueous TriEGME solutions ranging from 10-100% FSII by volume.

Karl Fischer Study

Figure 9 is a simple schematic of the Karl Fischer titration along with the governing reaction of titration:
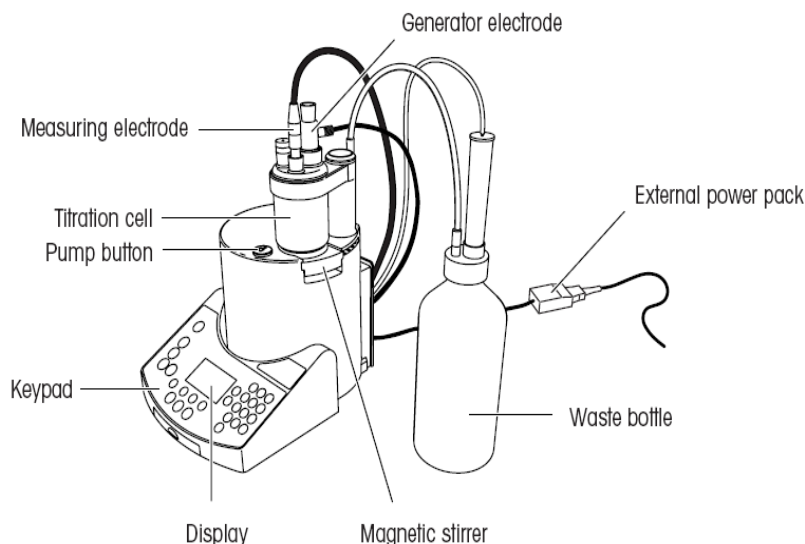
Figure 9. Simple, labeled schematic of the Karl Fischer titration instrument

$$ROH + SO_2 + RN \rightarrow (RNH) \cdot SO_3R$$
$$(RNH) \cdot SO_3R + 2RN + I_2 + H_2O \rightarrow (RNH) \cdot SO_4R + 2(RNH)I$$
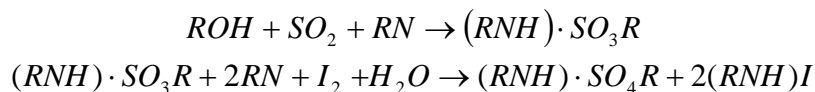
In coulometry, the iodine is titrated electrochemically by anodic oxidation:
$$2I^- \rightarrow I_2 + 2e^-$$
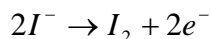
500 mL standard solutions of concentrations (0.02, 0.06, 0.1, 0.15, 1.19, and 1.57) volume percent of TriEGME and DiEGME in 5237 Jet A-1 fuel were prepared. 10 mL samples were then spiked with approximately a 2:1 ratio of fuel and excess water and well mixed using a Fischer Scientific Touch Mixer Model 231 hypersonic mixer. After the samples were well mixed for five minutes, and solution equilibrium was achieved, they were transferred to an L-K Industries Trans-A2115NH centrifuge for phase separation based on the relative density of the fuel mixture and free water. After the

excess water had been separated from solution, 1 mL samples from the bulk solution were taken via a clean syringe and tested using the Mettler Toledo DL39 Karl Fischer apparatus.

<u>Static Partitioning Studies</u>

This experimental system required six 2.0 L Nalgene Teflon-FEP, P/N 4301-2000

separatory funnels in which the fuel/water/FSII mixtures were placed. The separatory

funnels allow use of low water concentrations while the Teflon surface inhibits water

adhesion. The temperature of the mixture was influenced only by the ambient

environment which saw minimal fluctuations and stayed at a relative range of 20 to 23°C.
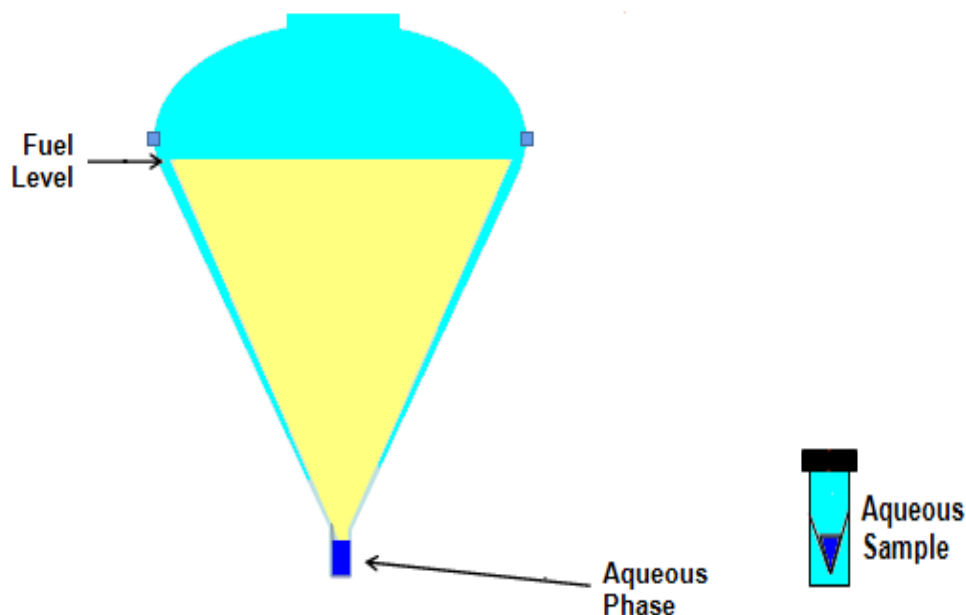
Figure 10. Schematic of the experimental Teflon separatory funnel

The experimental set-up required 130 ppm free water injected to the bottom of the

separatory funnel while pouring 1500 mLs of 0.1% vol binary mixture of FSII and

Jet A-1 fuel gently over the free water bottom layer to minimize mixing. A simple

schematic of the experimental set is shown on Figure 10. After desired time intervals

were achieved, the free water phase at the bottom of the separatory funnel was taken by

opening the funnel's bottom valve using a 3.0 mL cylindroconical glass collection vial.

The quantification of the dissolved DiEGME and TriEGME concentration in water was performed via the use of a Reichert Model AR200 digital refractometer. The method uses the relationship between concentration of the FSII in the water and the resulting refractive index of the mixture to perform the quantitation. The refractometer was calibrated using standard solutions of FSII and water. The calibration range of the refractometer was from 0-100% with a refractive index from 1.3300-1.4262 and 1.3300-1.4376 $\pm$ 0.0001 for DiEGME and TriEGME, respectively.

"SALEMS" Experiments

The experimental system which was devised by the researchers at the University of Dayton Research Institute comprised of the following: 2.0 L Teflon separatory funnel (Nalgene, Teflon-FEP, P/N 4301-2000), two thermocouples (T-type, 1/32" dia), two capillary sample lines (PEEK, 1/16" o.d., 0.020" i.d), and one Teflon ejector tube. The fluid ejector tube consisted of a 5/16" i.d teflon tube. One thermocouple and sampling line was positioned at the bottom of the separatory funnel immersed in the aqueous phase of the fuel/FSII/water mixture while the other sampling line and thermocouple located at the midpoint of the mixture level constituting the fuel phase. The Teflon nozzle was located approximately 1" above the aqueous mixture level and collectively, the thermocouples and lines were held in place with a rubber stopper. The separatory funnels were first filled with 1500 mL of 5237 jet fuel, and dosed with the approximate amounts of DiEGME/TriEGME concentration and mixed. The fluid was then sampled to verify the initial DiEGME/TriEGME concentration and the initial water content. Gas chromatography with mass selective detection (GC-MS) was used to determine DiEGME and or TriEGME concentration using extracted ion area response. The accuracy of this technique was approximately ±10% of the absolute concentration (West et al., 2009). The aqueous phase DiEGME or TriEGME concentration at the completion of testing was determined using the Reichert Model AR200 digital refractometer. The required water volume for injection was determined based on the desired target and initial dissolved water content of the fuel. The separatory funnels were placed into a Cincinnati Sub-Zero Model Z8 environmental chamber capable of temperature control within the range of -73$^{\mathrm{o}}$C to +190$^{\mathrm{o}}$C (±1°C).

During sampling, these lines were connected to 3.0 mL cylindroconical glass collection vials which were used to collect the fuel and aqueous samples by drawing liquid with the assistance of a vacuum pump. A fixed ramp rate of 5°C/hour was implemented to allow sufficient time for partitioning of DiEGME and or TriEGME into the aqueous phase while also allowing the testing to be conducted within a reasonable time frame. Total experimentation duration, including ramped cooling, was approximately 17 hours which provided a minimum equilibrium time of approximately three hours at the final temperature of -47°C. A schematic of the SALEMS apparatus is shown below in Figure 11.
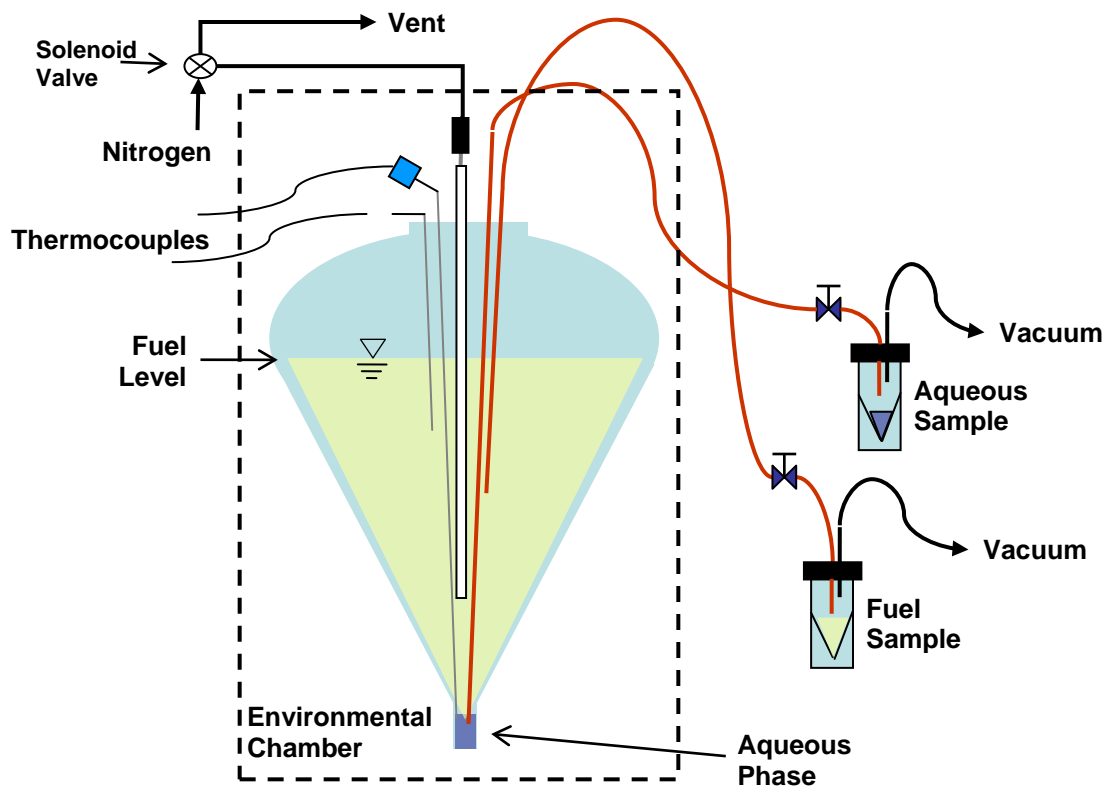
Figure 11. Schematic of the SALEMS apparatus; dotted lines indicate the environmental chamber (West et al., 2009)

Surface Tension Study

Experimental measurements were performed for a range of volume ratios of aqueous TriEGME, and neat Jet A-1 fuel in order to determine the interfacial surface tensions of the respective phases. Measurements were performed using a Fisher Surface Tensiomat, Model 21. The instrument has a platinum-iridium ring with the circumference of 6.04 cm that is suspended from a counter-balanced lever-arm. The arm is clamped to a stainless steel wire that holds it horizontal by torsion. For measurements between the liquid and air, the ring is initially immersed in the liquid and the arm and ring are raised by increasing the torsion in the wire. The tensiomat measures the force (dynes/cm) required to pull the ring free from the surface film of the liquid. Interfacial surface tension of two liquids is measured by either pulling the ring from the denser phase into the less dense, or pushing the ring from the less dense liquid into the denser liquid. The apparent surface tension is measured during testing; the absolute surface tension is calculated by multiplying by a correction factor. The tensiomat is factory-calibrated; the calibration is verified by analyzing a liquid of known surface tension (i.e., water). The accuracy of the method was approximately ±10%. The precision between duplicate measurements was approximately ± 10%.

Characterization of MDA using HPLC-MS

Calibration and characterization of MDA and MDA-Cu complexes were performed using an Agilent Technologies Liquid Chromatograph Time of Flight Mass Spectrometer (LC/MSD TOF) Model G1969A.

The LC method consisted of:

Mobile Phase: 95% CH_3OH + 0.1% (vol) Acetic Acid

　　　　　　5% De-Ionized H_2O

Injection Volume: 5 μL

Needle Wash in Flush Port for 20 seconds using mobile phase CH_3OH + 0.1% (vol) Acetic-Acid

Run Time: 10 minute

Post Time: 1 minute

Binary Pump SL Flow Rate: 0.3 ml/min

Ion Source: Dual ESI

LC Stream: MS

Dual ESI (Seg)

　　　Gas Temp: 350°C

　　　Drying Gas: 11 l/min

　　　Nebuliser: 50 psig

Dual ESI (Expt)

　　　VCap: 3500 V

　　　Capillary: 0.008 μA

　　　Chamber: 0.00 μA

MS TOF

　　　Fragmenter: 200 V

　　　Skimmer: 65 V

　　　OCT 1 RF Vpp: 250 V

Column: Agilent Zorbax (5 μm) 4.6 mm ID x 250 mm SB-C8

CHAPTER III

RESULTS AND DISCUSSION

FSII Property Measurements:

Equilibrium Dissolution of TriEGME & DiEGME

Fuel system icing inhibitors are injected into military jet fuels to prevent the free water present in solution from forming ice crystals which can plug fuel lines and filters. This is important because aerospace fuels are subjected to low temperature conditions during high altitude operation. Since FSII additives are required to remain in solution under all fuel conditions, studies were performed to compare the solubility of TriEGME and DiEGME as a function of temperature over the temperature range of -47 to 20°C. The soluble FSII concentration was measured by GC after exposure to excess levels. Figure 12 shows the measured solubility of TriEGME and DiEGME as a function of temperature with the solubility of TriEGME and DiEGME at -25°C, -40°C and -47°C expanded in the inset plot for clarity.
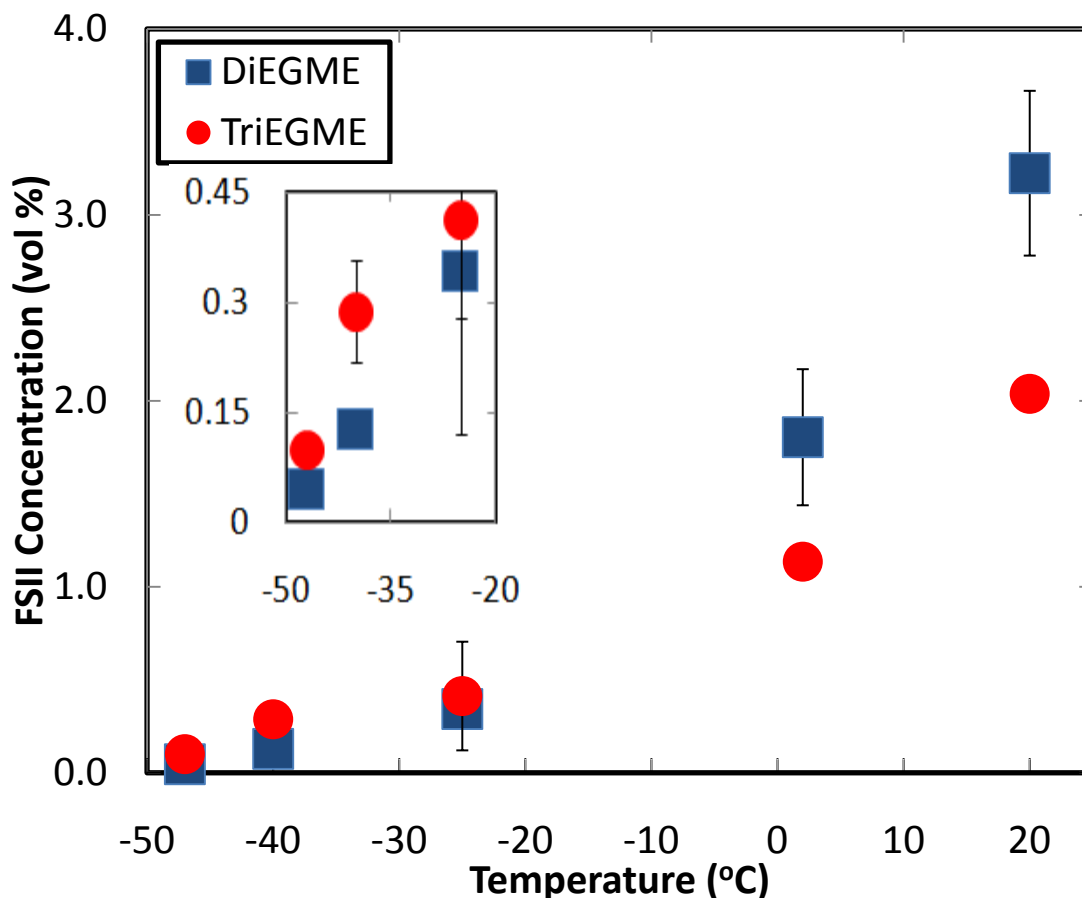
Figure 12. Solubility of TriEGME and DiEGME as a function of temperature

The figure shows that as temperature decreases, so does the solubility of both TriEGME and DiEGME. At temperatures below -25°C, TriEGME and DiEGME exhibit similar solubility levels in fuel. Most importantly, at -47°C TriEGME and DiEGME have equilibrium concentrations of 0.100 ± 0.005 and 0.045 ± 0.004 vol %, respectively. These solubility levels are at or below the specification procurement levels for JP-8 fuels. These data indicate that there may be concerns with FSII additives coming out of solution at low temperatures. The data shows that TriEGME should be less likely to precipitate and cause fuel system fouling at very low fuel temperatures. This is, however, somewhat unexpected as TriEGME has a higher molecular weight and melting point than DiEGME and should therefore be more likely to precipitate at low temperatures.

Freeze Point Determination Using DSC for DiEGME & TriEGME

Differential Scanning Calorimetry (DSC) was used to measure the ability of FSII additives to suppress water from freezing. The knowledge of FSII/water mixture freeze points is essential in determining the proper dosage of FSII for adequate low temperature protection. DSC is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. In these experiments, the samples are first cooled through the liquid-solid transition exotherm and then subsequently heated until the sample transitions back to the liquid phase exhibiting an endothermic response. The DSC response during heating only is shown in Figure 13 for TriEGME/water mixtures. The endothermic peak temperatures were used to construct a freeze point curve for FSII-water mixtures as shown in Figure 15.
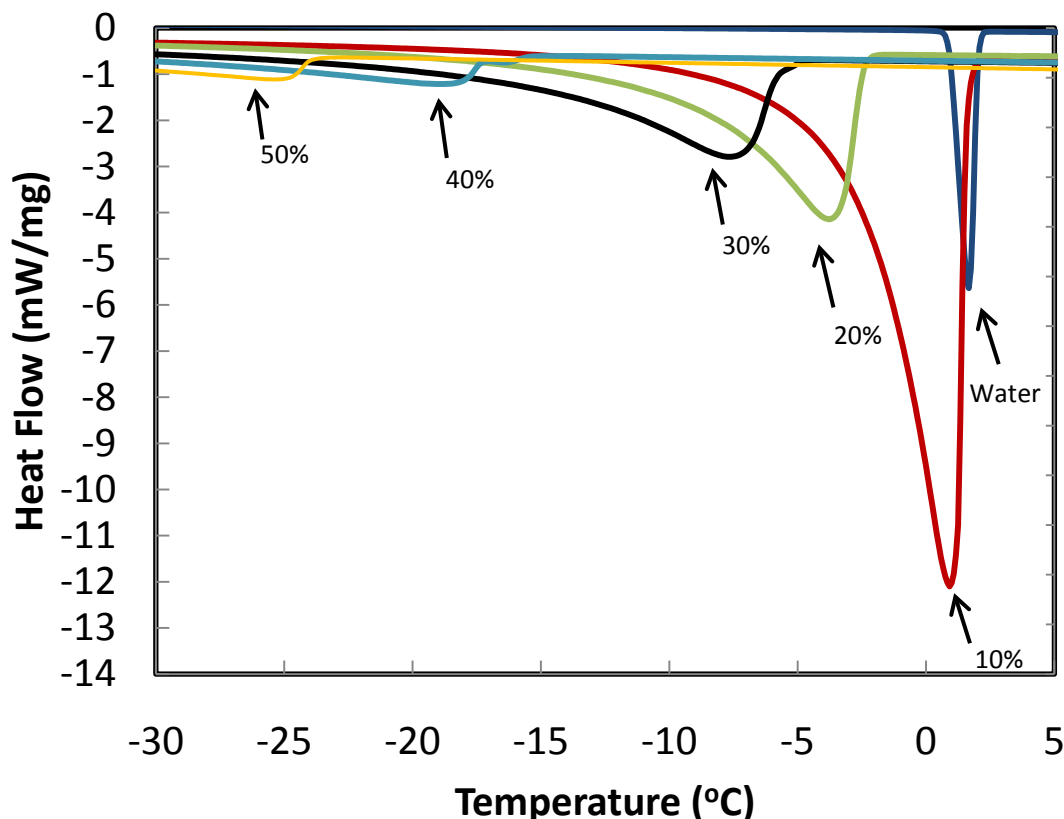
Figure 13. Endotherms of aqueous TriEGME as a function of concentration (vol %) using Differential Scanning Calorimetry

It proved to be difficult to measure the freeze point of aqueous TriEGME/water mixtures above 60 vol % as the endotherms were too broad and the signal to noise ratio was too low to adequately determine the phase transition temperature. The DiEGME/water mixture data for concentrations of 55 and 60% in Figure 14 were taken from experiments conducted using the Standard Test Method for Freeze Point of Aqueous Engine Coolants ASTM D1177 method. This method involved submerging the aqueous phase sample into a cooling bath and measuring the temperature at which the sample phase transitions from liquid to solid. The freeze point was measured by monitoring the temperature during solid to liquid phase change of the sample. Phase changes occur isothermally; therefore when temperature readings plateau or do not

change with respect to time and influx of heat, the freeze point of the aqueous sample is

determined to be at that temperature.
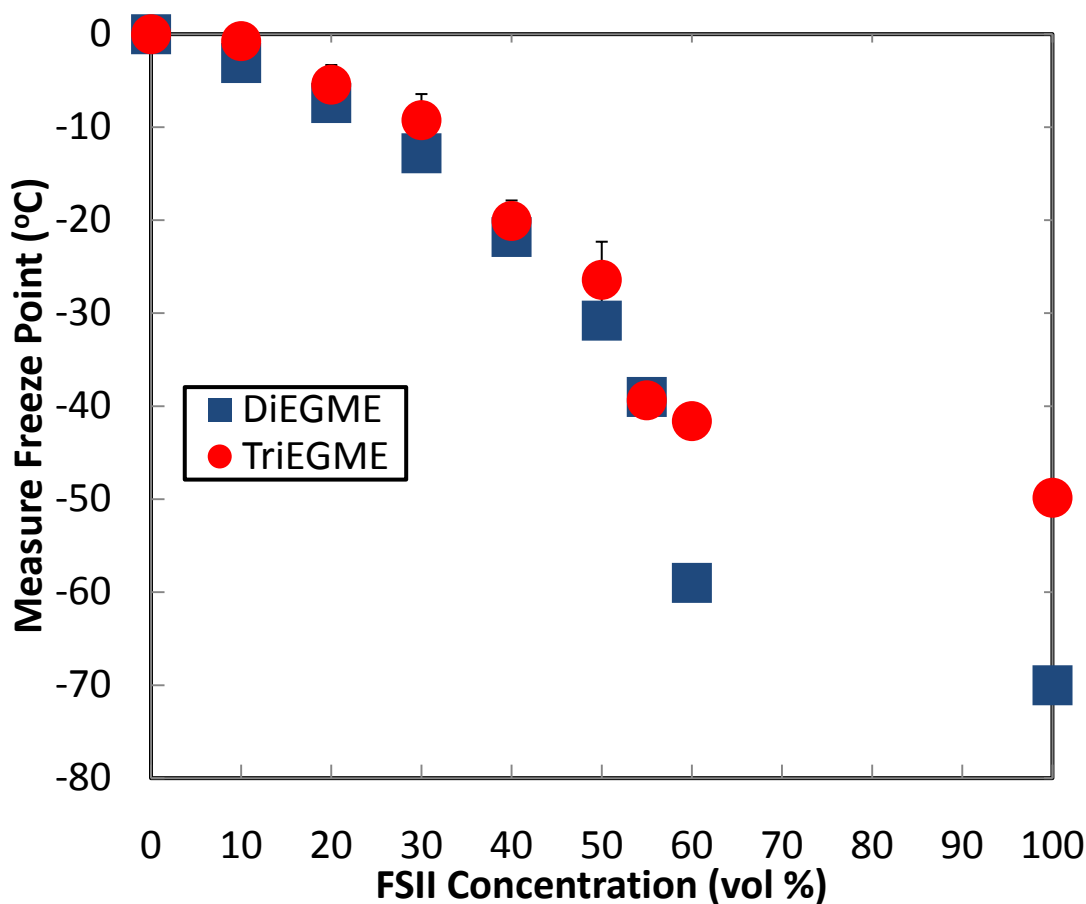
Figure 14. Freeze points of FSII/water mixtures by DSC and ASTM-D1177

The freeze points of DiEGME and TriEGME mixtures are very similar up to 55

vol %. At 60 and 100 vol % concentration, the freeze points of DiEGME and TriEGME

deviate by nearly 15 degrees with DiEGME having the lower freeze point temperature. It

is therefore suspected that either a eutectic point is reached within the 60-100 vol %

range where the freeze point may decrease and subsequently increase with increasing

FSII concentration, or that the freeze point continues to decrease as it approaches

100 vol % maintaining the approximate 15 degree difference between DiEGME and

TriEGME/water mixtures.

Low Temperature Viscosity Determination of TriEGME

Fuel system icing inhibitors partition into the free water present in fuels, forming a separate FSII/water mixture phase. This FSII/water phase is relatively viscous and may have different flow ability characteristics (DeWitt et al., 2005). The Tannas Scanning Brookfield Plus Two Viscometer was used to determine the TriEGME/water mixture viscosity with respect to temperature and concentration. The viscosity profiles upon cooling for the various aqueous TriEGME/water mixtures are shown in Figure 15.
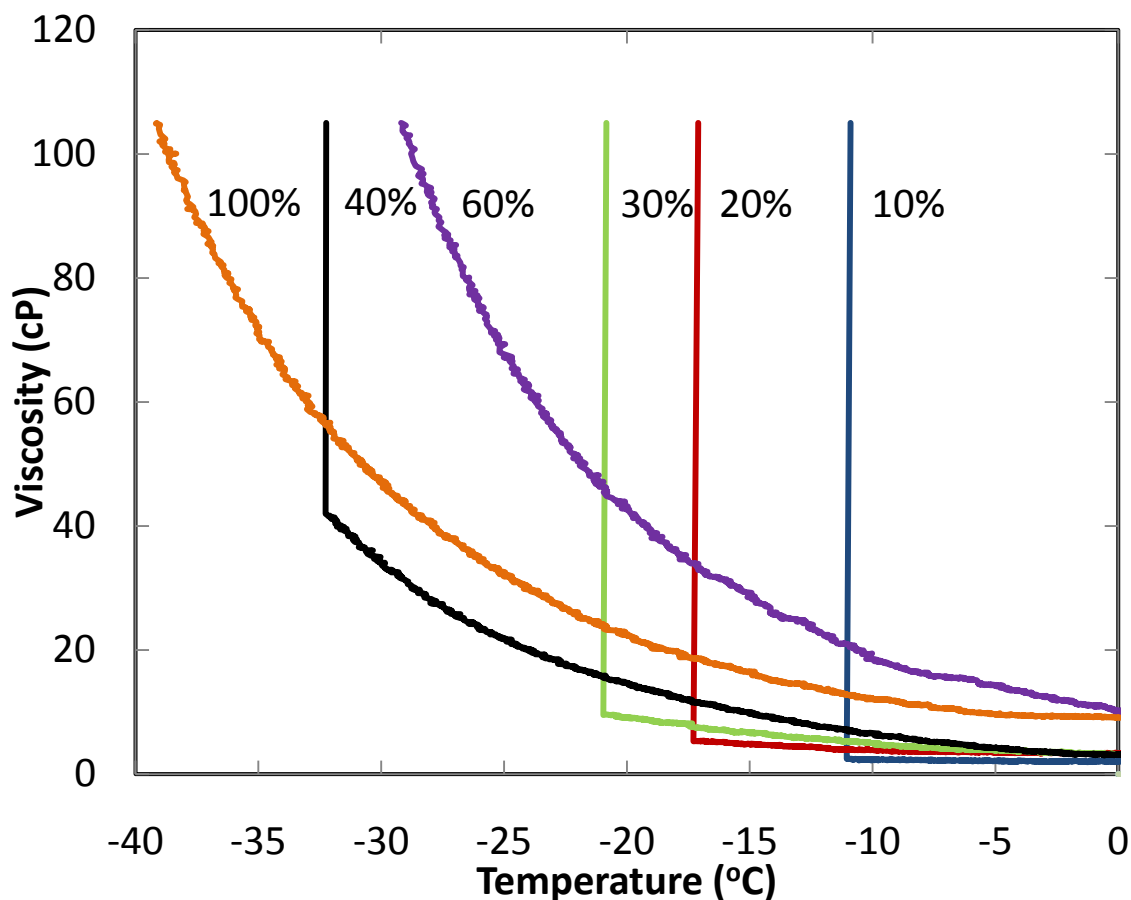
Figure 15. Viscosity profile for the cooling cycle of 10-100% by volume TriEGME in water

According to Figure 16, as the temperature decreases, the viscosity of TriEGME at different concentrations increases. Unfortunately, the Tannas Scanning Brookfield Plus Two viscosity measurements were made up to a viscosity of 105 cP. During the cooling cycles of experiments conducted for TriEGME/water mixtures with a concentration greater than 40 vol %, the characteristic knee of the TriEGME/water mixture curves were not exhibited, but rather a continual increase in viscosity until data was unable to be recorded.

Effect of TriEGME and DiEGME on Equilibrium Dissolution of Water

Fuels always have low levels of dissolved water at a concentration range up to 100 ppm. This dissolved water, at low temperatures, precipitates and freezes causing major problems. Polar compounds have been implicated in increasing water solubility in fuel and glycol ethers may be sufficiently polar to increase water solubility. The effects of initial fuel/FSII concentration on water solubility were studied. Figure 16 illustrates the water solubility as a function of FSII concentration in fuel. In these studies, water was mixed with the fuel/FSII mixtures under room temperature conditions for five minutes, centrifuged and the dissolved water was measured using the Karl Fischer titration instrument.
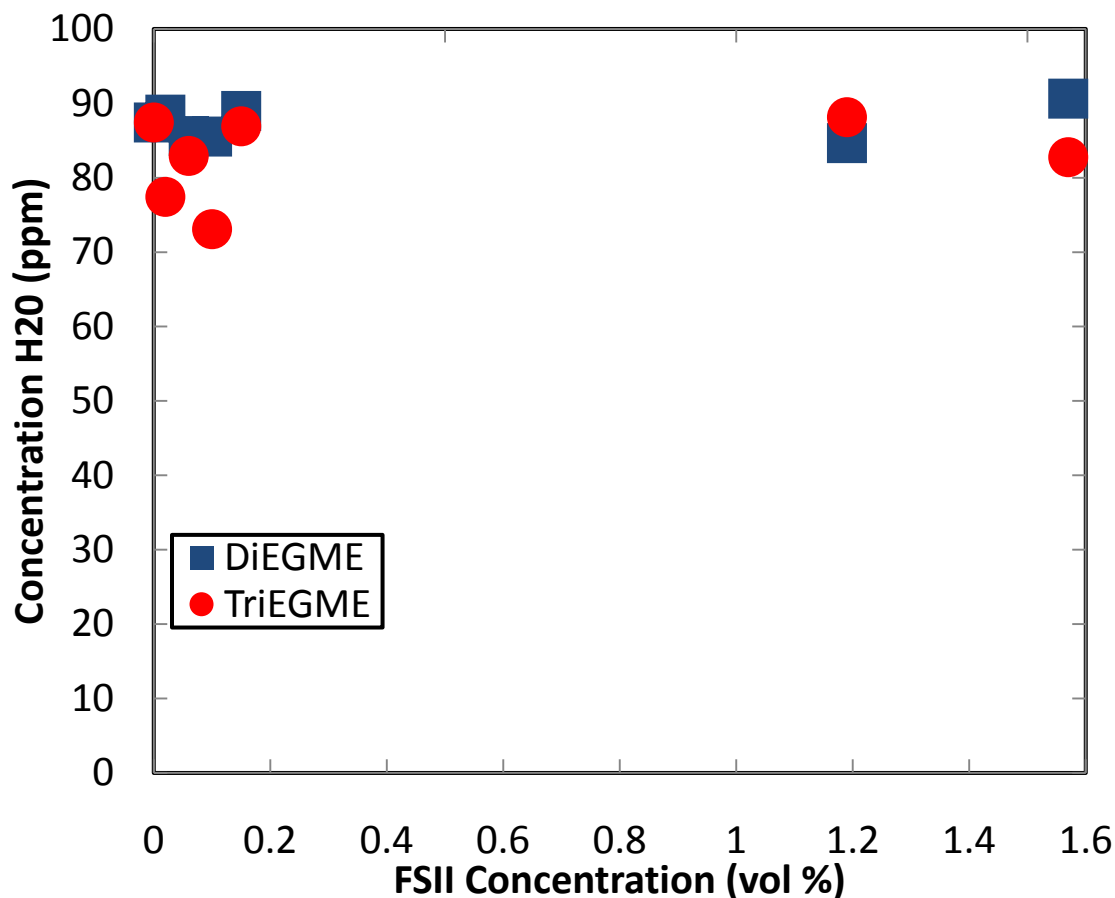
Figure 16. Comparison of water solubility as a function of TriEGME and DiEGME concentrations in Jet A-1 fuel

The results indicate that the dissolved water concentration was within the range of 84-91 ppm for DiEGME/fuel mixtures and 72-87 ppm for TriEGME/fuel mixtures over the range of 0-1.6 vol %. The plot indicates that water solubility does not increase with FSII concentration. A limitation to this work is that only room/ambient temperatures were studied. As fuels are exposed in the environment to a wide range of temperatures, it is desirable to measure the effect of FSII on water solubility over a wide range of temperatures.

Static Aqueous Phase Partitioning of DiEGME & TriEGME

Most icing inhibition studies are conducted under equilibrium conditions where the partitioning of FSII between the fuel and aqueous phases is in equilibrium. It is essential that FSII candidates, such as TriEGME, partition into the fuel phase at a rate fast enough to inhibit freezing. The determination of the rate by which DiEGME and TriEGME partition from the fuel to the aqueous phase was measured by exposure of a water phase to a fuel phase with added FSII. The separatory funnels used in this study allowed the use of low water concentrations (130 ppm) while the Teflon surface inhibited water adhesion. The temperature of the mixture was influenced only by the ambient environment which saw minimal fluctuations and stayed at a range of 20-23°C. Figure 17 shows the percent DiEGME and TriEGME in the aqueous phase as a function of time at room temperature.
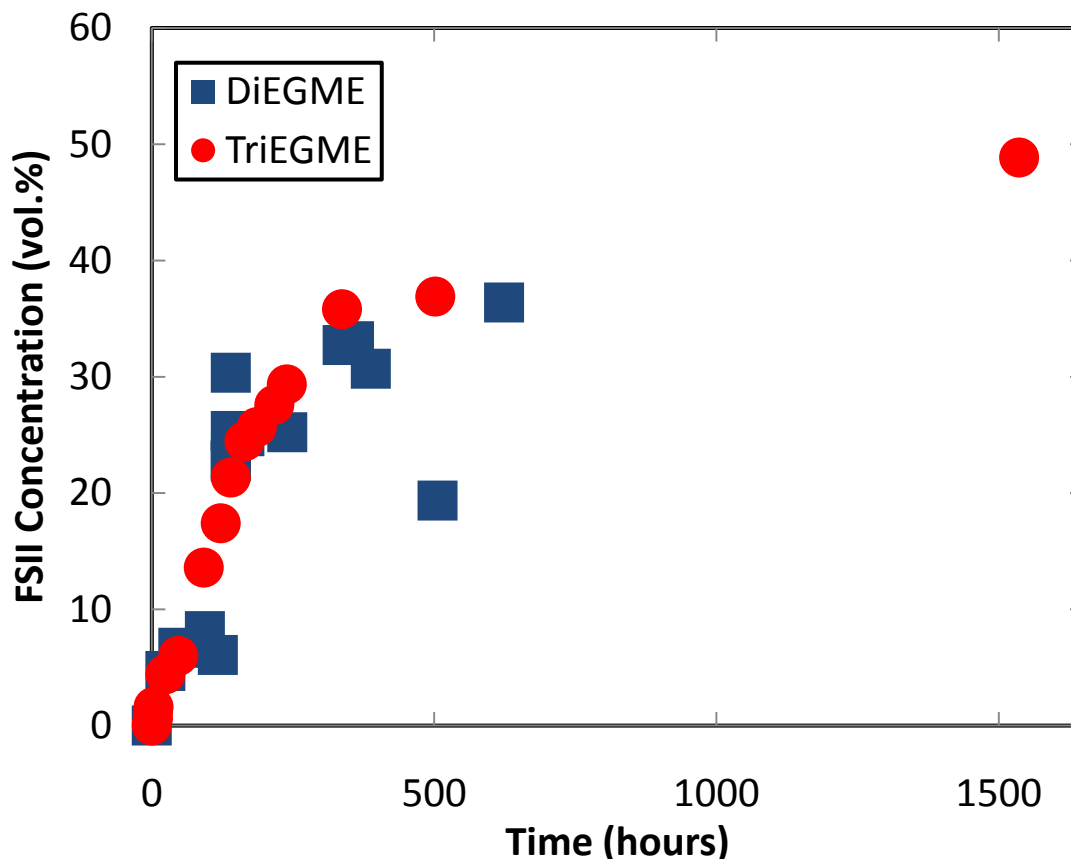
Figure 17. Concentration of DiEGME and TriEGME in the aqueous phase with respect to time

130 ppm of free water was injected to the bottom of the separatory funnel while pouring 1500 mL of 0.1% vol binary mixture of FSII and Jet A-1 fuel. For DiEGME, experimentation was conducted for a period of four weeks and TriEGME a period of eight weeks. The static partitioning rates for both DiEGME and TriEGME were very similar. Surprisingly, these static partitioning rates were extremely slow, especially considering the fuel temperature cool down rate in aircraft tanks during flight. Fuel temperature decreases occur over the course of a few hours of flight, thus it is apparent that new water droplets, during fuel cooling, need to rapidly equilibrate with the FSII present. This may occur during water precipitation and/or the partitioning rate may be increased by agitation of the fuel by boost pumps and flight vibration.

Temperature Dependant Partitioning of DiEGME & TriEGME in water using
Sub-Ambient Liquid Equilibrium Measurement System (SALEMS)

Previous studies of equilibrium partitioning of FSII additives between fuel and

aqueous phase were conducted by the University of Dayton Research Institute using Sub-

Ambient Liquid Equilibrium Measurement System or SALEMS (West et al., 2009).

Figure 18 is a plot of the equilibrium behavior of DiEGME concentration in fuel and

aqueous phase as a function of temperature where the data taken by the University of

Dayton Research Institute is from ambient to -30°C.
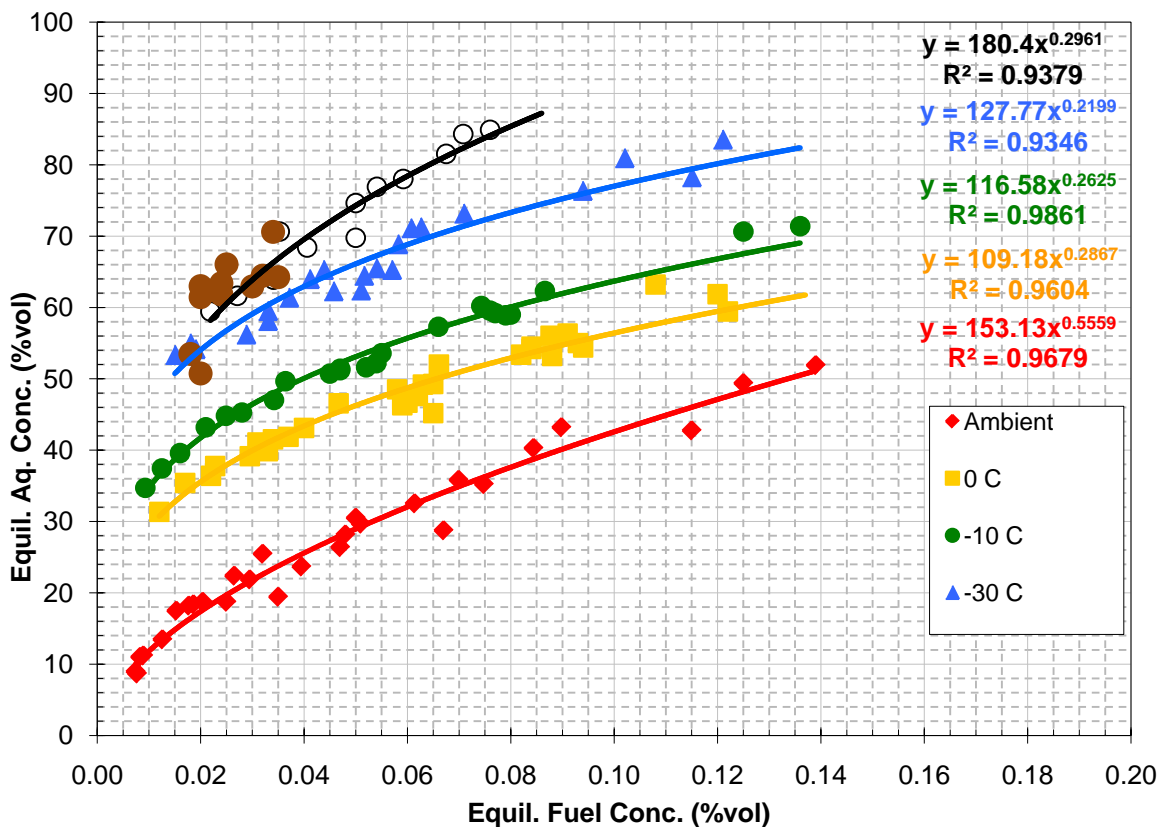
Figure 18. DiEGME concentration in fuel and aqueous phases with respect to
temperature and total water concentration ranging from 130-560 ppm (West et al., 2009)

According to Figure 18, the equilibrium concentration of DiEGME in the aqueous

phase increases as temperature decrease. This is desirable as a larger concentration of

FSII is required in order to prevent the free water from freezing at low temperatures while at higher temperatures a substantial FSII concentration in the aqueous phase is not required. This trend is also desirable for TriEGME and in Figure 19 a plot of the equilibrium behavior of TriEGME concentration in fuel and aqueous phase with respect to a 300 ± 1 ppm total water concentration is shown. Also plotted is the DiEGME partitioning at -47°C which shows the two FSII additives exhibit similar behavior at this temperature.
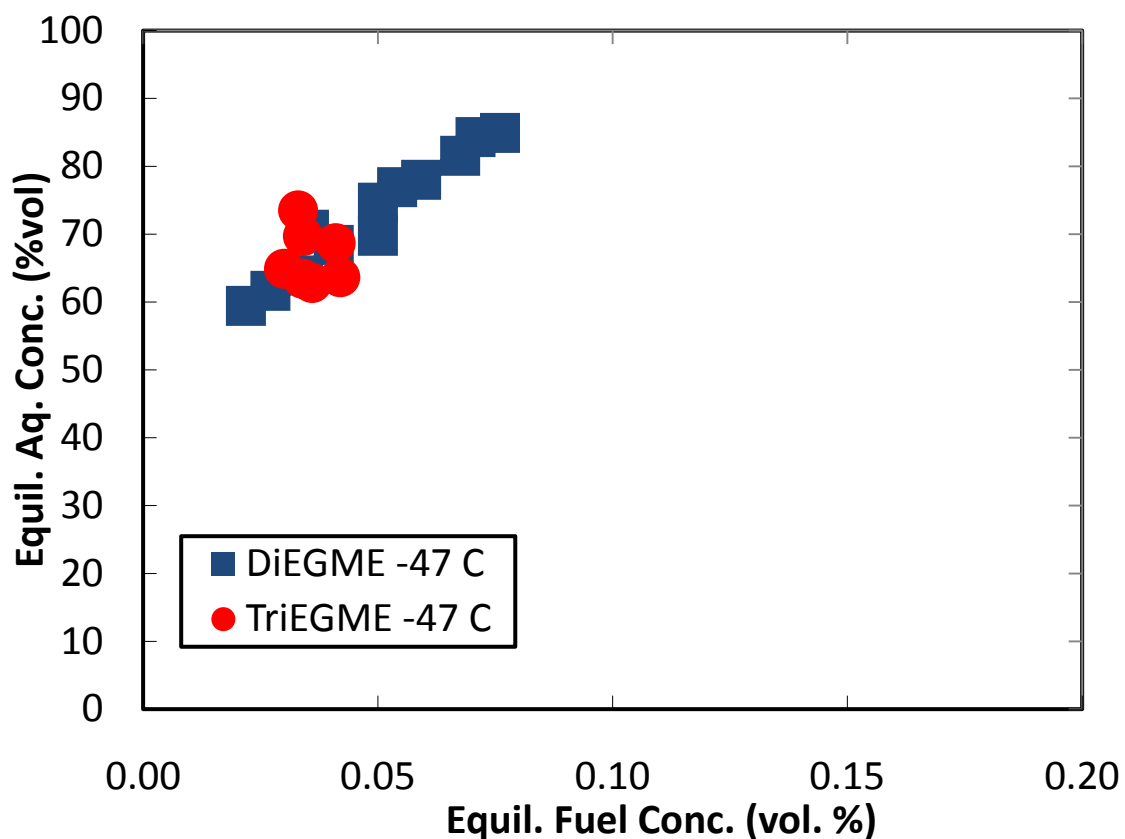
Figure 19. SALEMS data for equilibrium concentration of DiEGME and TriEGME in fuel and aqueous phases at -47°C

This behavior shows that TriEGME has the proper partitioning behavior to function as a satisfactory icing inhibitor agent for low temperature applications. However, in real fuel systems, a water bottom would likely already contain FSII due to previous exposure to multiple fuel volumes containing FSII additives. Therefore, multiple exposures to FSII/fuel lessen the need for higher FSII concentrations in fuel.

MDA Studies:

Metal Deactivating Additives (MDA)

Fuel system metal deactivating additives, MDA, are injected into fuels to prevent metal catalyzed oxidation reactions by chelating or binding dissolved metal ions into an MDA-metal complex. MDA is considered very efficient at this free metal ion scavenging and also works by passivating the catalytic active sites on the metal surfaces (Striebich et al, 2000). Aerospace fuels contain trace amounts of metal ions such as copper, iron, and zinc which may have strong pro-oxidant capabilities. The oxidation of fuel consists of a mechanism of chemical chain and branching reactions where fuels deteriorate, resulting in fouling of surfaces and plugging of nozzles and valves (Zelesnik, 1995). This process involves the production of species which accelerate autoxidation, such as peroxides, where the degradation process initially proceeds slowly only to gradually accelerate until a maximum rate is reached. This rate phenomenon is better termed autoxidation or catalytic autoxidative degradation (Zabarnick et al., 2007). Solving this problem lies in not only limiting the oxygen rate, but also limiting the ability of the trace metals to initiate this catalytic autoxidative degradation mechanism. Where past studies, such as the derivatization technique proposed by Striebich et al (2000) using GC-MS, focused on characterizing the MDA compound in solution, here we develop a new technique using the HPLC-MS instrument. Specifically, a method designed for determination of the concentrations of metal compounds present in fuels along with the speciation of those metals is desired. Such a method would not only help researchers determine the identity of the metal, but the form it takes upon speciation when metal complexes are formed.

Because metal deactivating additives are important for fuel thermal stability, studies were performed to quantitatively and qualitatively characterize MDA, Cu(II)AcAc , and the MDA-Cu(II) complex in solution. Concentration standards for the studied compounds were tested in methanol and 5237 Jet A-1 fuel. Table 3 shows the m/z ratios associated with the multiple forms of MDA, Cu(II)AcAc and the MDA-Cu(II) complex and the associated ions that were studied via HPLC-TOFMS. The m/z values shown are the calculated molecular weights of the chemical species studied using the HPLC-MS instrument in which MDA, Cu(II)AcAc and the MDA-Cu(II) complex were characterized with either an H^+ or Na^+ ion upon ionization. The table illustrates the MDA-Cu(II) complex characterized at three different charges ($^+1$, $^+2$ and $^+3$). Only the $^+1$ charge was found to exist during the MDA-Cu(II) complex reaction where MDA attacks the substrate copper center of Cu(II)AcAc and removes the copper ion.

Table 3. MDA, Cu(II)AcAc, MDA-Cu(II) Complexes with Associated Ions Studied

Compound	Form (1), m/z	Form (2), m/z	Form (3), m/z
MDA+H$^+$	MDA+H$^+$ (283.1441)		
MDA+Na$^+$	MDA+Na$^+$ (305.12600)		
MDA-Cu+H$^+$	MDA-Cu+H$^+$ (344.05805)	MDA-Cu+H$^+$ (345.06588)	MDA-Cu+H$^+$ (346.0737)
	MDA-Cu+H^{2+} (172.5367)	MDA-Cu+H^{2+} (173.03658)	MDA-Cu+H^{2+} (173.54049)
	MDA-Cu+H^{3+} (115.35754)	MDA-Cu+H^{3+} (115.69348)	MDA-Cu+H^{3+} (116.02942)
MDA-Cu+Na$^+$	MDA-Cu+Na$^+$ (366.04055)	MDA-Cu+Na$^+$ (367.04782)	MDA-Cu+Na$^+$ (368.0556)
	MDA-Cu+Na^{2+} (194.51461)	MDA-Cu+Na^{2+} (195.01852)	MDA-Cu+Na^{2+} (195.52244)
	MDA-Cu+Na^{3+} (137.33948)	MDA-Cu+Na^{3+} (137.67542)	MDA-Cu+Na^{3+} (138.01136)
Cu(II)AcAc+H$^+$	Cu(II)AcAc+H$^+$ (262.02609)		
	Cu(II)AcAc+H^{2+} (131.51668)		
	Cu(II)AcAc+H^{3+} (88.01355)		
Cu(II)AcAc+Na$^+$	Cu(II)AcAc+Na$^+$ (284.00803)		
	Cu(II)AcAc+Na^{2+} (153.49863)		
	Cu(II)AcAc+Na^{3+} (109.99549)		

Knowing an accurate m/z value for any chemical species is crucial to identifying the compound when using the HPLC-MS instrument. This is especially important when studying a mixture such as Jet A-1 fuel where many hydrocarbon species exist with similar m/z values. An experimenter can easily misinterpret or confuse a hydrocarbon species for the chemical species of interest such as MDA when studying fuels, therefore the proper molecular weight must be established before qualitative and/or quantitative

analysis can be conducted. Along with the proper molecular weight, a mass defect is needed for characterization using the HPLC-MS software. This mass defect is essentially the range in which the HPLC-MS software looks for a particular m/z of a species. For example, when characterizing MDA with a proton ion, the calculated m/z value is 283.1441. For the HPLC-MS instrument, a range between 283.1-283.2 was used to search for that particular ion at that particular m/z ratio. Table 4 shows the compound, m/z ratio and characterization range for each of the chemical species studied using the HPLC-MS.

Table 4. Characterization Range and m/z ratio for Each Species Studied Using HPLC-MS

Compound	m/z	Range
MDA+H$^+$	283.1441	283.1-283.2
Cu(II)AcAc+H$^+$	262.02609	262.0-262.1
(1) MDA-Cu+H$^+$	344.05805	344.0-344.1
(2) MDA-Cu+H$^+$	345.06588	345.0-345.1
(3) MDA-Cu+H$^+$	346.0737	346.0-346.1
MDA+Na$^+$	305.126	305.1-305.2
Cu(II)AcAc+Na$^+$	284.00803	284.0-284.1
(1) MDA-Cu+Na$^+$	366.04055	366.0-366.1
(2) MDA-Cu+Na$^+$	367.04782	367.0-367.1
(3) MDA-Cu+Na$^+$	368.0556	368.0-368.1

MDA Studies in Methanol Matrix:

<u>Characterization of N,N'-disalicylidene-1,2-propanediamine (MDA)</u>

While striving to develop a method for characterizing the speciation of metals in

fuels, the first step in this process was to determine if the HPLC-MS instrument had the

ability to ionize and characterize MDA in methanol. Methanol standards were prepared in

conjunction with a methanol/water/acetic acid mobile phase in order to provide the best

environment for successful analyte separation. This first step was essential in determining

whether standards tested in a fuel matrix were feasible given that quantification and

instrument sensitivity would theoretically be easier to accomplish in a methanol solvent

(Cech and Enke, 2001). Without the luxury of referencing chromatographic techniques

from previous studies, a standard method using the HPLC-MS instrument was

constructed where the mobile phase consisted of HPLC grade methanol spiked with

0.1 vol % acetic acid. One goal of adding acetic acid to the mobile phase solution was to

encourage ionization at the electrospray source. Another goal was to also provide an

environment for MDA, Cu(II)AcAc and the MDA-Cu(II) complex to elute from the

column upon separation. This is essential as previous studies indicated that depending on

the column material, highly surface active species may not elute properly, if at all,

without the addition of acid to the mobile phase solution (Taylor and Synovec, 1994).

Standards were prepared with a concentration range between 0-80 µg/L and

0-10,000 µg/L in methanol and tested in order to quantify a relative response with respect

to concentration. The concentration ranges were tested to determine the upper and lower

quantification limit for MDA. Figure 20, shows the relative response of MDA as a

function of concentration from 0-80 µg/L.
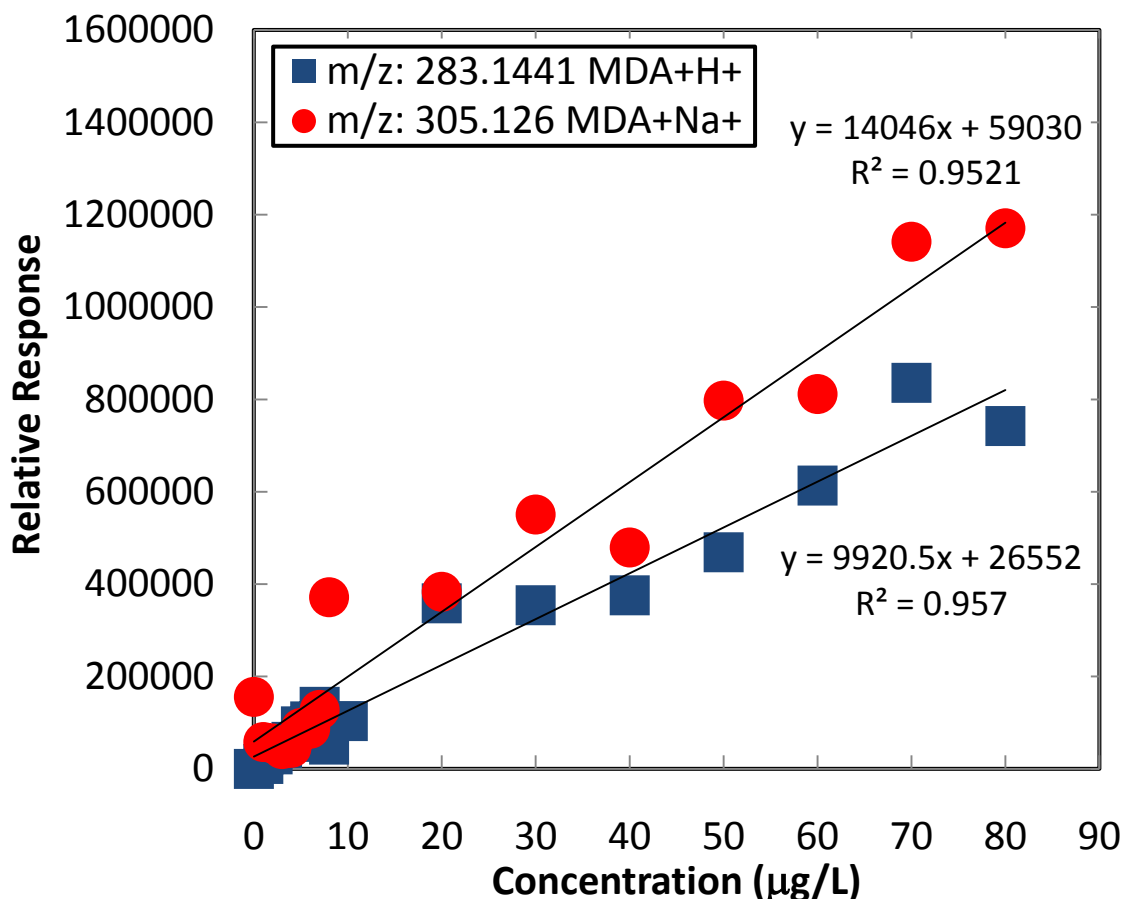
Figure 20. Response of MDA as a function of concentration

The figure shows the calibration of MDA with respect to a proton and sodium ion

attached during the ionization process using HPLC-MS. The sodium ion form, gave a

relative response approximately 50% greater than that of the protonated form of MDA as

indicated by comparing the figure plots and calibration slope equations. This increase in

response is perhaps due to the greater affinity of Na^+ ions than H^+ ions to be attached to

the analyte during the ionization process at the electrospray source. A higher response

may correlate to an ease of ionizability of MDA with a sodium ion attached (Cech and

Enke., 2001). Figure 20 indicates that the protonated form of MDA can be characterized

and calibrated by the HPLC-MS instrument as a function of concentration and has a lower detection limit of less than 1 µg/L. It is assumed to have a lower detection limit below 1 µg/L because at 1 µg/L, the MDA response is at 10,000+ counts. Such a high response at this concentration leads to speculation that a response can be found at lower concentrations. For the sodiated form of MDA, a non-zero response for blank standards or baseline was recorded at 155,000 counts. This non-zero response led to the sodiated form of MDA having a detection limit of 8 µg/L. It is assumed to have this detection limit based on the baseline response of 155,000 counts. A possible reason for this non-zero response for blanks may be due to the large mass range for the sodiated form of MDA using the mass hunter qualitative software for the HPLC-MS analysis. The m/z range of 305.1-305.2 may indeed be too large and a suggested narrowing of this range for future analysis is recommended. A narrower range may eliminate the non-zero response factor for blank standards and thus provide a detection limit below 8 µg/L.
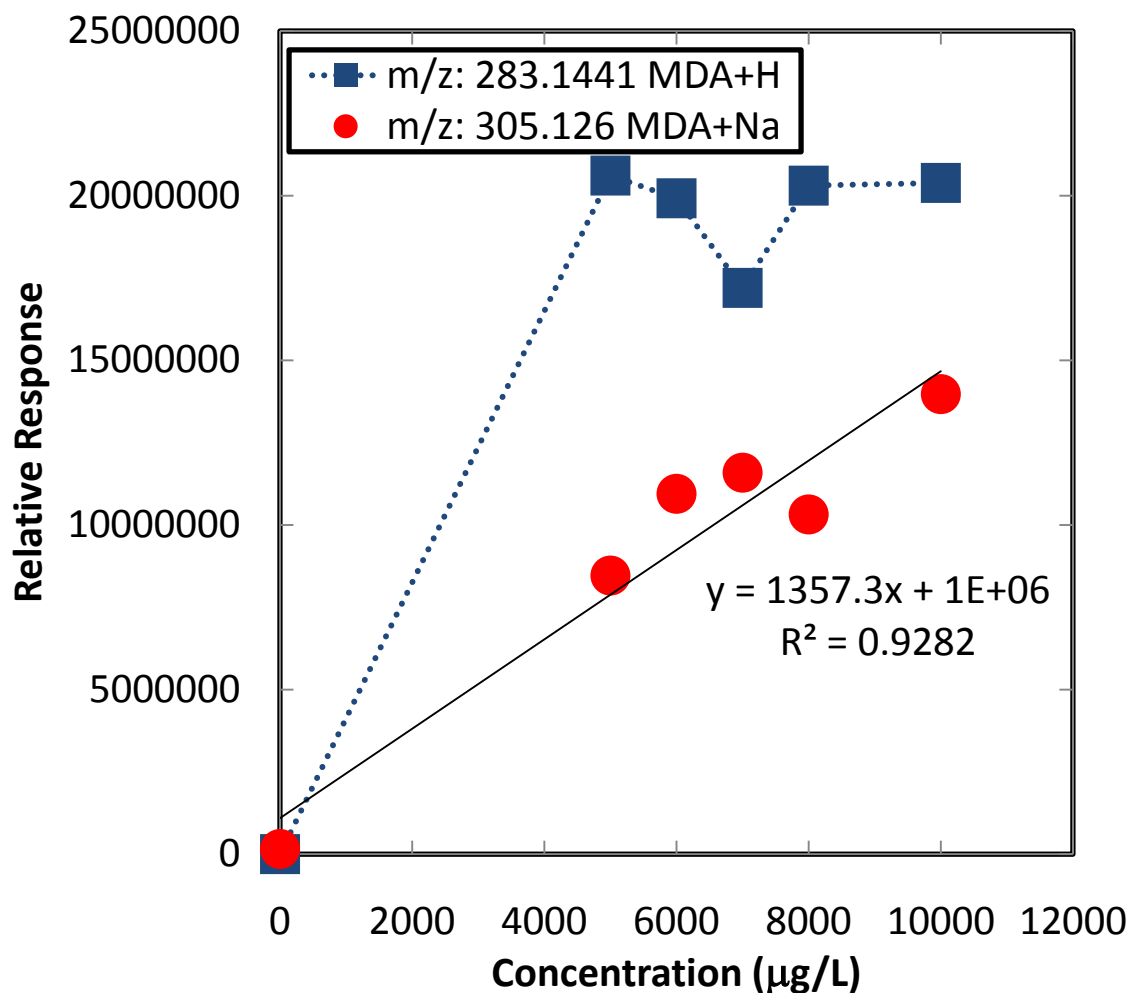
Figure 21. Response of MDA as a function of higher concentration

Figure 21, shows the relative response level of MDA as a function of

concentration from 0-12000 µg/L in order to determine the upper limit of quantification.

This figure shows that the protonated form of MDA has an upper detection limit that may

be at a concentration below 5,000 µg/L as the response has leveled off at this

concentration. The sodiated form of MDA has an upper detection limit above 10,000

µg/L with an R^2 value of 0.928 which shows a linear response factor. These results are

essential in the method development of characterizing MDA in fuels since fuel samples

will be diluted in methanol when analyzed in the HPLC-MS instrument.

Characterization of Copper(II)Acetoacetonate (Cu(II)AcAc)

The ability to measure metal concentration during fuel testing is of interest to fuel researchers (Striebich et al., 2000, Pederson et al., 1949). With copper being a strong catalyst for the catalytic oxidative degeneration of fuels, experiments were designed using Cu(II)Acetoacetonate as a copper source for characterization. The ability to identify metals such as copper using the HPLC-MS instrument will provide researchers information on the complexation state of these metals in solution (Taylor and Synovec 1994). Standards were tested using the HPLC-MS instrument in order to quantify a relative response with respect to concentration of Cu(II)Acetoacetonate. Figure 22, illustrates the relative response level of Cu(II)AcAc as a function of concentration from 0-10,000 μg/L.
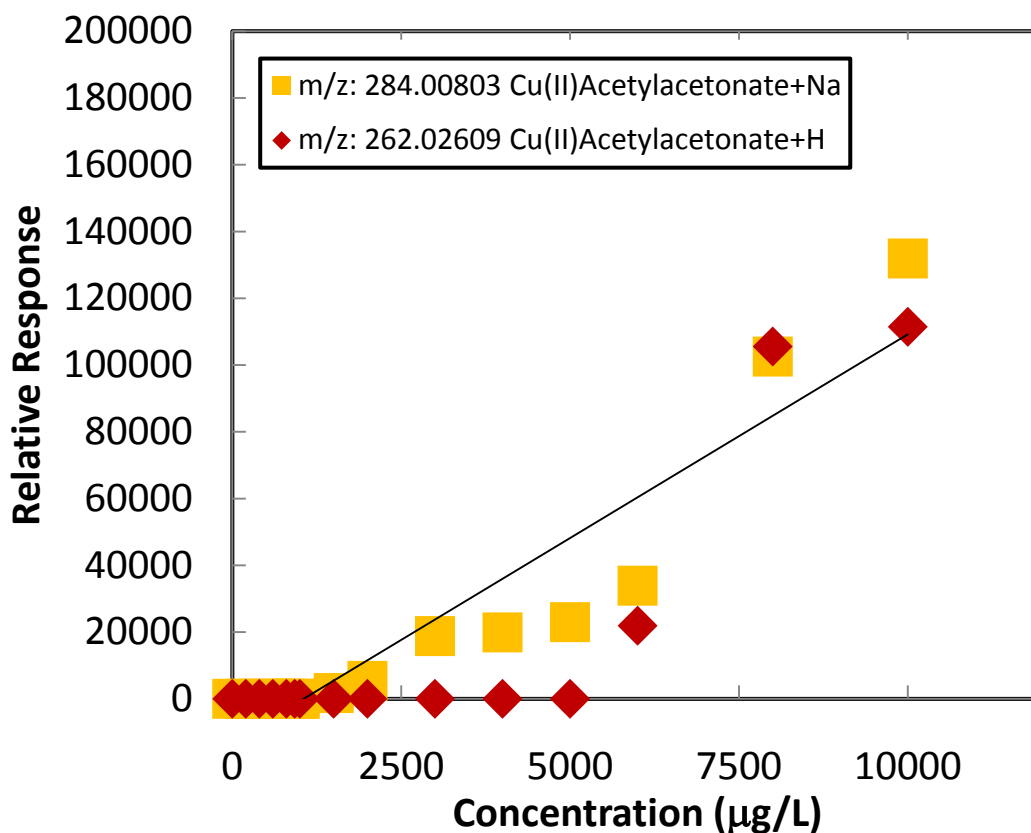
Figure 22. Response of Copper(II)Acetoacetonate as a function of concentration

The figure shows the calibration of Cu(II)AcAc with respect to proton and sodium ions attached during the ionization process using HPLC-MS. For m/z: 262.02609, the response has been multiplied by fifty for higher resolution and qualitative differentiation. The relative response for the sodiated form of Cu(II)AcAc is nearly sixty times that of the protonated form of Cu(II)AcAc. The results also show that as concentration increases, so does the relative response of Cu(II)AcAc which indicates a proportional relationship between response and concentration for both the sodiated and protonated forms of Cu(II)AcAc. With R^2 values of 0.8736 and 0.7236 however, the calibration of Cu(II)AcAc in methanol is poor. For the protonated form of Cu(II)AcAc, the detection limit is 6,000 µg/L and has a maximum response of only 2,200 counts at 10,000 µg/L. For the sodiated form of Cu(II)AcAc, the detection limit is 1,500 µg/L and has a maximum response of 130,000 counts at 10,000 µg/L. Lower detection limits are required for fuel analysis in the range of 0-50 µg/L which is typically where copper concentrations exist for aerospace fuels. A possible reason for such high detection limits is that Cu(II)AcAc could perhaps be a surface active chemical species due to the presence of functional groups such as the carboxyl. Although derivatization techniques have demonstrated success when dealing with such compounds by silylating surface active functional groups, it is highly unlikely such a technique could work for Cu(II)AcAc without breaking up the compound (Striebich et al., 2000). Another way to address the sensitivity issue of Cu(II)AcAc is to increase the acetic acid concentration of the HPLC-MS mobile phase solution.

This could help decrease the absorption of Cu(II)AcAc onto the HPLC-MS column and better elute the analyte for analysis (Taylor and Synovec, 1994). The ability, however, to characterize Cu(II)AcAc in solution is nevertheless an important first step in and shows promise for speciating other metal complexes.

Characterization of MDA-Copper(II) Complex

With the success of characterizing MDA and Cu(II)Acetoacetonate in methanol, subsequent tests were performed in order to determine if the HPLC-MS instrument could characterize the MDA-Cu(II) complex in methanol. The ability to characterize the MDA-Cu(II) complex in methanol may also give insight into the kinetics, reaction mechanism and overall reactivity of MDA and its ability to scavenge metals in solution (Cech and Enke, 2001). Standards were prepared with a concentration range between 0-80 μg/L in a methanol solvent where MDA and Cu(II)AcAc were reacted in solution at equimolar concentrations. These standards were then tested using the HPLC-MS instrument in order to quantify a response with respect to concentration.

Figure 23. Response of MDA-Copper(II) complex (protonated) as a function of concentration

Figure 23 shows the relative response of three isotopes of the MDA-Cu(II) complex in methanol with a proton ion attached during ionization. The first isotope of the MDA-Cu(II) complex, m/z: 344.05805, is one of three stable isotopes of the complex while m/z's 345.06588 and 346.0737 are the other two. Beyond the ability to calibrate the MDA-Cu(II) complex and its associated isotopes, an observation from these experiments has been the chemical structure based on the m/z and the relative response ratios between the three isotopes of the complex. The greatest response factor is present for the isotope with m/z: 344.05805 and the three dimensional structure can be found in Figure 7 of the

chapter one for reference. The characterized MDA-Cu(II) complex is formed where two hydrogens are displaced during the complexation reaction between MDA and Cu(II)AcAc. A ratio of 1:12 and 1:4 exists for the isotopes with m/z: 345.06588 and m/z: 346.0737 respectively when compared to the response of m/z: 344.05805. For m/z: 344.05805, the detection limit is less than 2 µg/L and has a maximum response of $100,000 \pm 9,000$ counts at 80 µg/L. For m/z: 345.06588, the detection limit is approximately 40 µg/L and has a maximum response of only $16,000 \pm 3,000$ counts at 80 µg/L. This isotope of the MDA-Cu(II) complex is obviously not very useful for low concentration calibrations, but for higher concentrations, the relative response trend seems to indicate it could be. For the isotope of MDA-Cu(II) complex, m/z: 346.0737, the detection limit is approximately 6 µg/L and has a maximum response of $48,000 \pm 1,400$ counts at 80 µg/L. This upward response trend with respect to concentration indicates an upper detection limit beyond 80 µg/L.
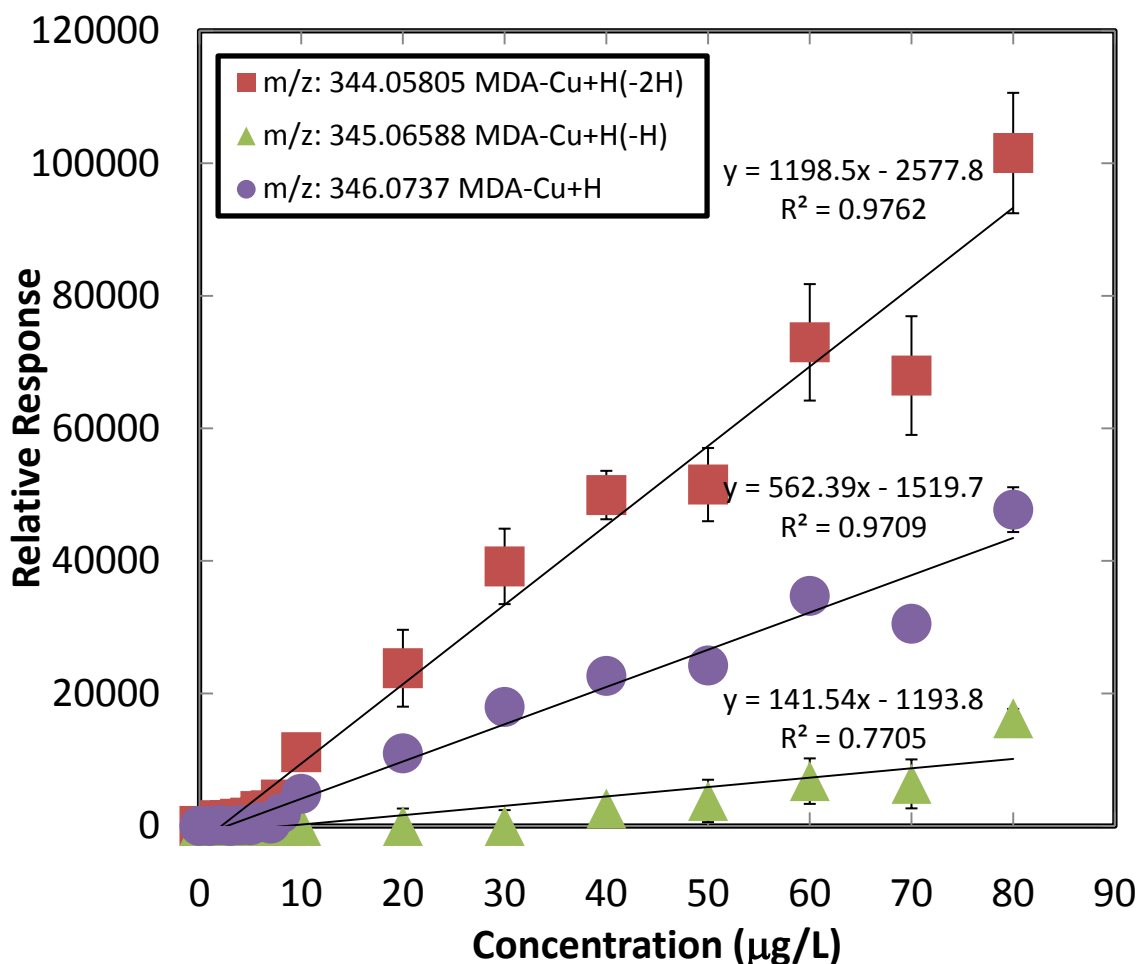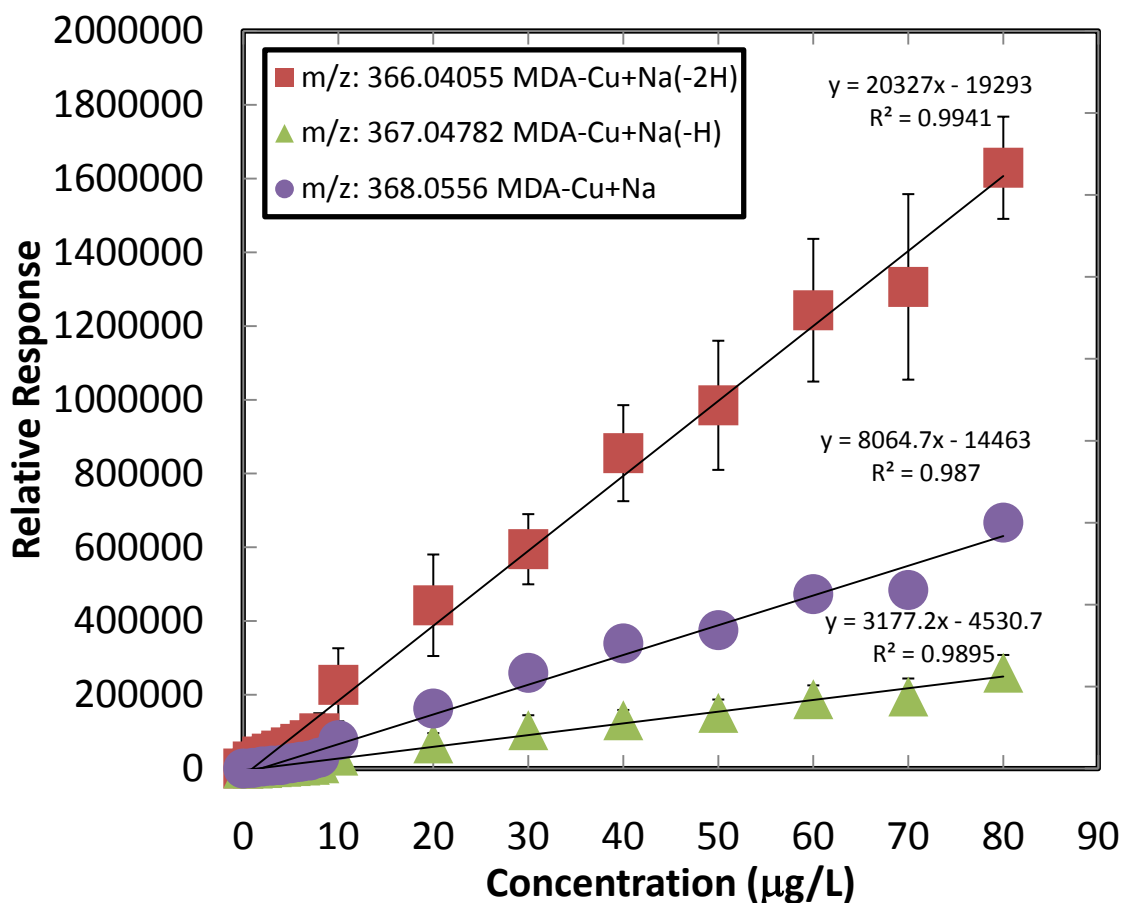
Figure 24. Response of MDA-Copper(II) complex (sodiated) as a function of concentration

Figure 24 shows the relative response of the MDA-Cu(II) complex in methanol with a sodium ion attached during ionization. Similar results were observed for the sodiated form of the complex when compared to the protonated form. A ratio of 1:9 and 1:4 exists for the complex with m/z: 367.04782 and m/z: 368.055660 respectively when compared to the response of the m/z: 366.04055 form. For the m/z: 366.04055, the detection limit is less than 1 µg/L and has a maximum response of $1,600,000 \pm 138,000$ counts at 80 µg/L. Compared to the MDA-Cu(II) complex with a proton ion, m/z: 344.05805, the response has sixteen times the intensity and better linearity with an R^2 value of 0.9941. For the m/z: 367.04782, the detection limit is approximately 40 µg/L and has a maximum response of only $260,000 \pm 21,000$ counts at 80 µg/L. For

the complex isotope with m/z: 368.0556, the detection limit is approximately 6 µg/L and

has a maximum response of $660,000 \pm 48,000$ counts at 80 µg/L. For both the protonated

and sodiated forms of the MDA-Cu(II) complex, the response for the isotope of m/z:

344.05805 and m/z: 366.04055 is nearly four times that of the isotopes of m/z: 345.06588

and m/z: 367.04782 respectively.

MDA Studies in Fuel Matrix:

<u>Characterization of N,N'-disalicylidene-1,2-propanediamine (MDA)</u>

Standards were prepared with a concentration range between 0-1,250 µg/L in

5237 Jet A-1 fuel and diluted 20:1 in methanol in order to quantify a relative response

with respect to concentration using the HPLC-MS instrument. The concentration ranges

were tested to determine the upper and lower quantification limit for MDA in a fuel

matrix. Figure 25, shows the relative response level of MDA as a function of

concentration from 0-1,250 µg/L.
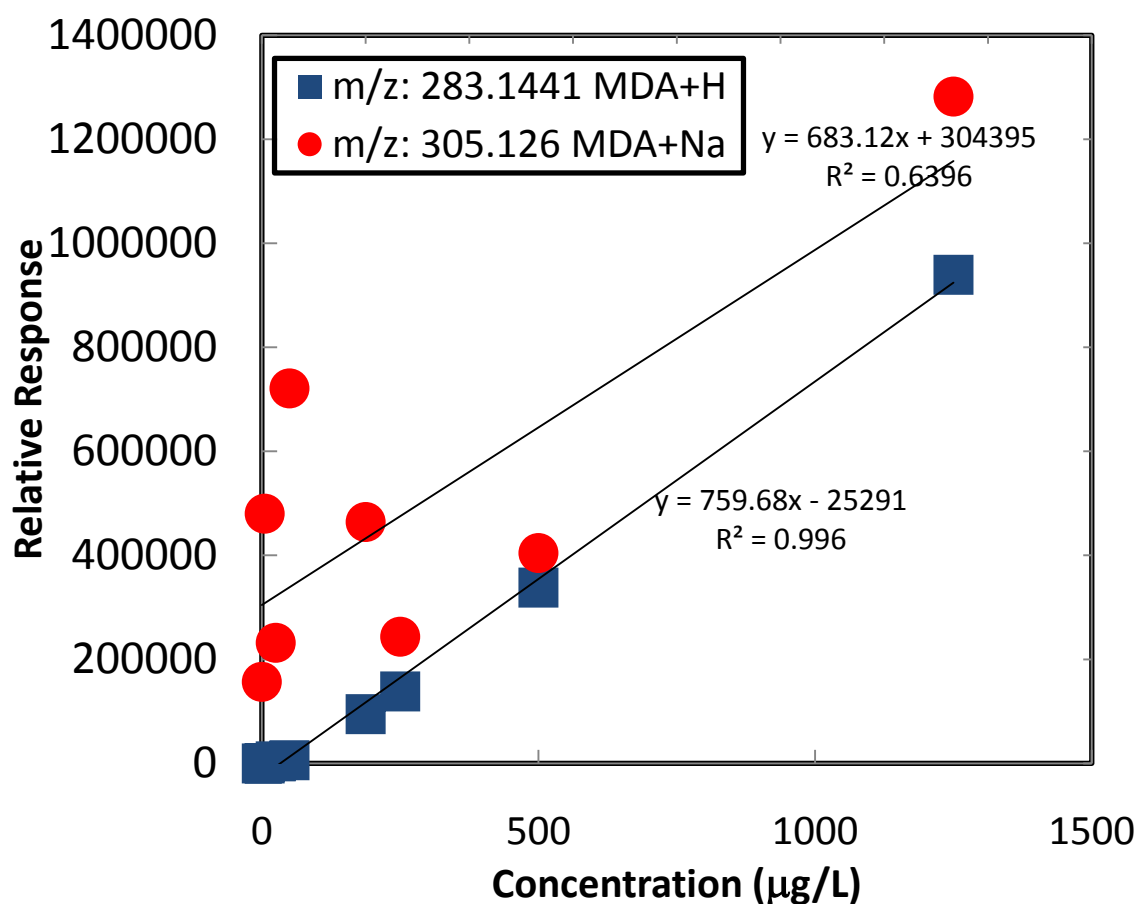
Figure 25. Response of MDA as a function of concentration

The figure shows the calibration of MDA with respect to a proton and sodium ion attached during the ionization process using HPLC-MS. The attached sodium ion form, gave a noisy relative response greater than that of the protonated form of MDA. The figure also shows that as concentration increases, so does the relative response of MDA which indicates a proportional relationship between response and concentration for the protonated form but not the sodiated form with R^2 values of 0.996 and 0.6396, respectively. For the protonated form of MDA, at concentrations greater than 25 µg/L, the response increases linearly to a maximum of approximately 940,000 counts at 1,250 µg/L. This indicates that the protonated form of MDA can be characterized and calibrated by the HPLC-MS instrument as a function of concentration and has a lower detection limit of 25 µg/L. For the sodiated form of MDA, a non-zero response for blank samples was recorded at 156,000 counts. This non-zero response for blank standards along with the varied response levels at different concentrations led to the unsuccessful calibration of the sodiated form of MDA. A possible reason for the response variability of the sodiated form of MDA is that Na^+ may perhaps be bound to other species in the fuel matrix, and thus not available to ionize (Cech and Enke, 2001).

Characterization of Copper(II)Acetoacetonate (Cu(II)AcAc)

Standards were tested using the HPLC-MS instrument in order to quantify a

relative response with respect to concentration of Cu(II)Acetoacetonate in a fuel matrix

from 0-500 μg/L. Both the proton and sodium ion forms gave a varied relative response

and as concentration increased the response factor varied $\pm$ 1,000 counts. The inability to

calibrate any form of Cu(II)AcAc within a fuel matrix may be attributed to the inability

to ionize properly or the fragmentation of both forms (protonated and sodiated) upon

ionization (Cech and Enke, 2001). This seems highly unlikely for the sodiated form of

Cu(II)AcAc as blank standards exhibited a non-zero response factor greater than those of

the concentrated standards. Although derivatization techniques have demonstrated

success when dealing with such compounds by silylating surface active functional

groups, it is highly unlikely such a technique could work for Cu(II)AcAc, however an

attempted is recommended (Striebich et al., 2000). Another way to address the sensitivity

issue of Cu(II)AcAc is to decrease the acetic acid concentration of the HPLC-MS mobile

phase solution. This could help limit the possible reaction between acetic acid and

Cu(II)AcAc where H^+ ions attack the carboxyate group of Cu(II)AcAc dissociating the

complex and forming copper byproducts.

Characterization of MDA-Copper(II) Complex

With the success of characterizing MDA, subsequent tests were performed in order to determine if the HPLC-MS instrument could characterize the MDA-Cu(II) complex in a fuel matrix. The ability to characterize MDA-Cu(II) complex in fuel may also give insight into the kinetics, reaction mechanism and overall reactivity of MDA and its ability to scavenge metals in a fuel solution (Cech and Enke 2001). Standards were prepared with a concentration range between 0-1,250 µg/L in a fuel matrix and diluted 20:1 in methanol where MDA and Cu(II)AcAc were reacted in solution at equimolar concentrations. These standards were then tested using the HPLC-MS instrument in order to quantify a response with respect to concentration.

Figure 26. Response of MDA-Copper(II) complex (protonated) as a function of concentration

Figure 26 illustrates the relative response of three isotopes of MDA-Cu(II) complex in fuel with a proton ion attached during ionization. The greatest response factor is present for the isotope with m/z: 344.05805. A ratio of 1:6 and 1:4 exists for the complex isotopes with m/z: 345.06588 and m/z: 346.0737 respectively when compared to the response of m/z: 334.05805. For the m/z: 344.05805, the detection limit is less than 25 µg/L and has a maximum response of 295,000 counts at 968 µg/L. For the m/z: 345.06588, the detection limit is approximately 190 µg/L and has a maximum response of only 53,000 counts at 968µg/L. This isotope of the MDA-Cu(II) complex is obviously not very useful for low concentration calibrations, but for higher concentrations, the

relative response trend seems to indicate it could be. For the isotope of MDA-Cu(II)

complex with m/z: 346.0737, the detection limit is approximately 25 µg/L and has a

maximum response of 125,000 counts at 968 µg/L. This upward response trend with

respect to concentration indicates an upper detection limit beyond 968 µg/L, however

such concentrations are not applicable to fuel analysis and therefore provide little use

beyond determining the upper detection for instrument capability purposes.
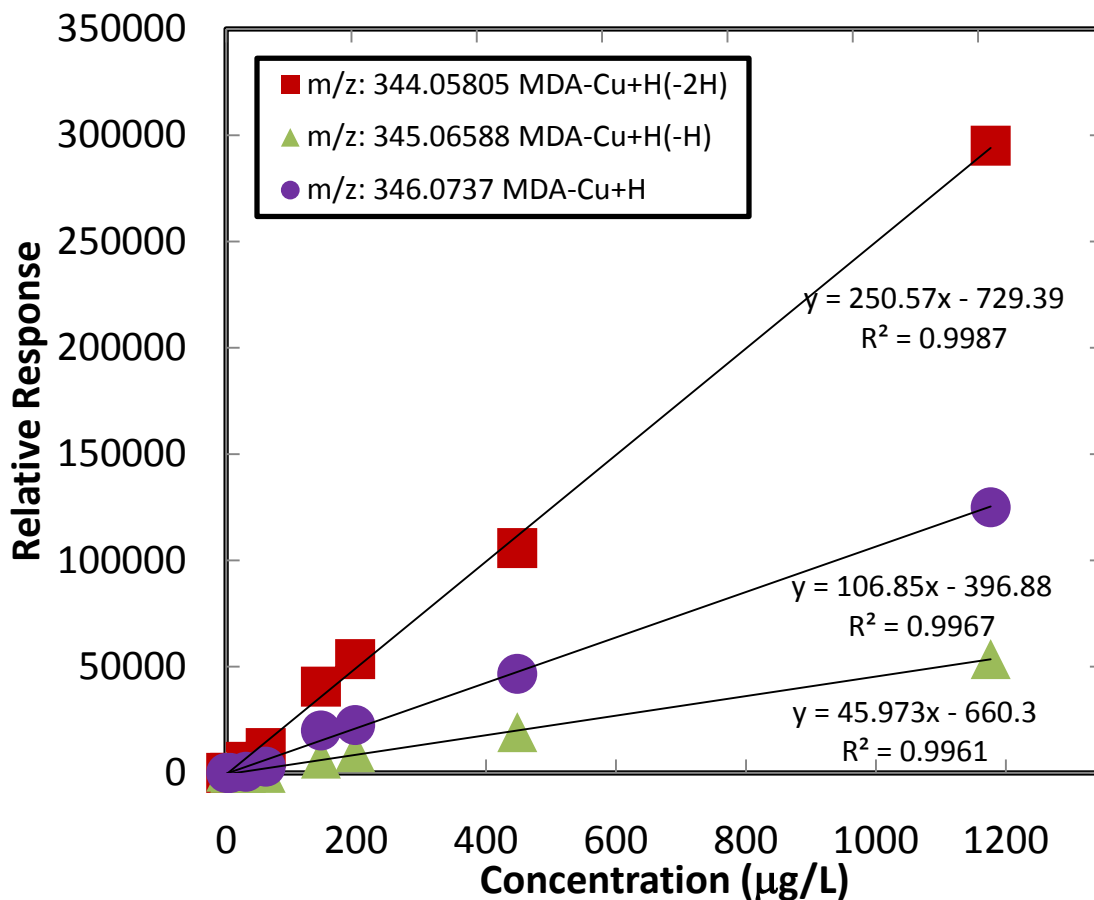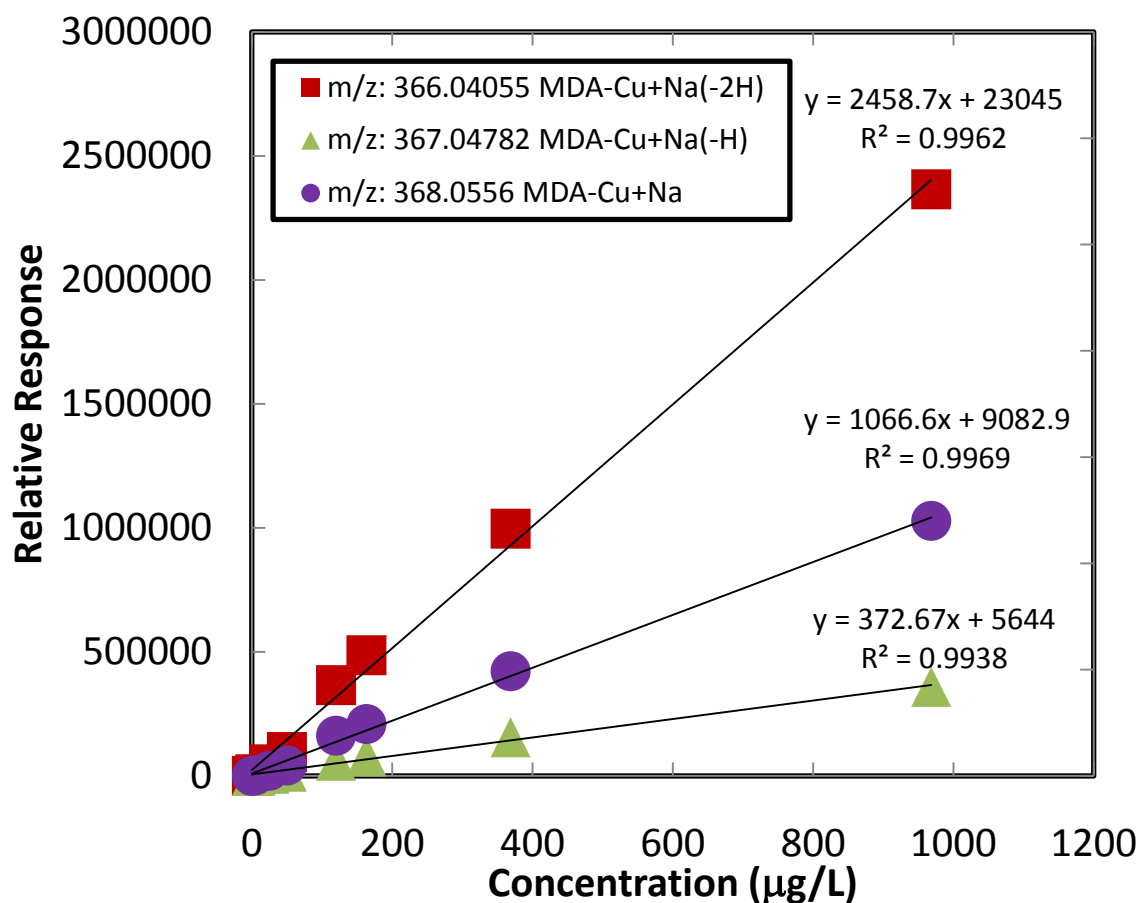

Figure 27. Response of MDA-Copper(II) complex (sodiated) as a function of
concentration

Figure 27 shows the relative response of the MDA-Cu(II) complex with a sodium

ion attached during ionization. The greatest response factor also exists isotope of the

complex with m/z: 366.04055. A ratio of 1:6 and 1:2 exists for the complex with m/z:

367.04782 and 368.05560 respectively when compared to the response of the m/z: 366.04055. For m/z: 366.04055, the detection limit is less than 5 µg/L and has a maximum response of 2,400,000 counts at 968 µg/L. Compared to the MDA-Cu(II) complex with a proton ion, m/z: 344.05805, the response has eight times the intensity with similiar linearity with R^2 values above 0.99. For the m/z: 367.04782, the detection limit is approximately 25 µg/L and has a maximum response of only 350,000 counts at 968 µg/L. For the isotope of MDA-Cu(II) complex with m/z: 368.0556, the detection limit is approximately 5 µg/L and has a maximum response of 1,020,000 counts at 968 µg/L. For both the protonated and sodiated forms of the MDA-Cu(II) complex, the response for the m/z: 344.05805 and 366.04055 is nearly four times that of the isotopes of m/z: 345.06588 and m/z: 367.04782 respectively.

Relative Mass Intensity Comparison of MDA-Cu(II) complex

Table 5. Calculated and Experimental Relative Mass Intensity for MDA-Cu(II) Isotopes

m/z	Isotope Form (Adduct)	Mass Intensity (Calculated)	Mass Intensity (Experimental)
344.05805	Protonated	100	100
345.06588	Protonated	18.4	$13.4 \pm 4.4\%$
346.07370	Protonated	44.6	$44 \pm 5.8\%$
366.04055	Sodiated	100	100
367.04782	Sodiated	18.4	$13.9 \pm 3.9\%$
368.0556	Sodiated	44.6	$41.4 \pm 3.7\%$

Table 6 shows the relative mass intensities of the isotopes characterized within the methanol and fuel matrix using the HPLC-MS instrument. The calculated relative mass intensity was compared to the relative mass intensity determined from experimental calibration curve slopes of the corresponding isotopes. This calculated relative mass intensity is based on a natural isotope abundance calculation created by David and John Manura of Scientific Instruments Inc., where the values are based on m/z's 344.05805 and 366.04055 for the protonated and sodiated forms respectively and every atom of the MDA-Cu(II) complex is integrated into the calculation. The similarity between the calculated and experimental relative mass intensities serves to further confirm the characterization of the MDA-Cu(II) complex isotopes using the HPLC-MS instrument.

Kinetic Study of MDA

Studies were performed in order to determine the efficiency of formation of MDA-Cu(II) complexation and the reaction time needed to reach equilibrium. The efficiency of MDA, as a function of percentage remaining copper, is shown in Table 5. At equimolar, (1:1) concentrations of MDA and Cu(II)AcAc, 30% of Cu(II)AcAc remains in solution while at (2:1) excess, no Cu(II)AcAc remains. The reaction for (1:1) ratio reaches equilibrium within the first day while the (2:1) excess reaction reaches equilibrium after approximately six days. Given that MDA is usually added to fuels in an excess far greater than 2:1, the results shown in Table 5 demonstrate that free copper is complexed within the fuel matrix and the reaction equilibrium is reached within a reasonably short time frame.

Table 6. %Cu(II)AcAc Remaining with Respect to Time and MDA:Cu(II)AcAc Ratio

Ratio	Days	% Cu Remaining
1:1	1	30% $\pm$ 7%
1:1	3	31% $\pm$ 6%
1:1	4	32% $\pm$ 1%
2:1	1	44% $\pm$ 9%
2:1	2	12% $\pm$ 5%
2:1	4	13% $\pm$ 6%
2:1	6	0% $\pm$ 3%
2:1	7	0% $\pm$ 2%

MDA Response Decline Study

Experiments were performed in order to determine the solution shelf life of MDA by measuring the change in response of MDA with respect to concentration and time. Standards for analysis were prepared with a concentration range between 0-1,000 µg/L in a fuel matrix and diluted 20:1 in methanol before analysis. These standards were then repeatedly tested over the span of approximately two weeks using the HPLC-MS instrument in order to quantify a response with respect to concentration.
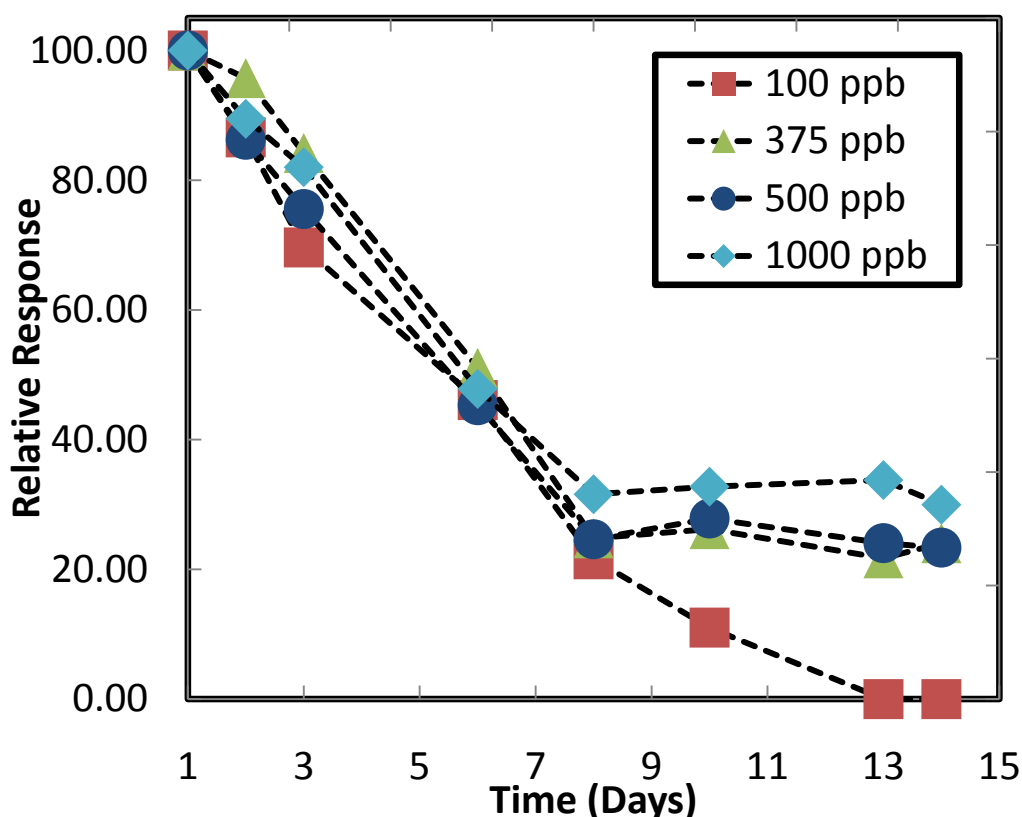
Figure 28. MDA response with respect to concentration and time

Figure 28 illustrates the relative response of MDA in fuel with a proton ion attached during ionization with respect to time and concentration. This change in response has a major effect when quantitating MDA and the MDA-Cu(II) complex based on the mole balance. The results reveal the decline in MDA response over time if it is not

complexed with metal and were observed for each of the concentrations studied. The fate of MDA in solution, however, is unclear as it could react with other hydrocarbon species within the fuel matrix or simply undergo surface adsorption.

CHAPTER IV

CONCLUSIONS

FSII Property Measurements:

An investigation focused on comparing the properties of TriEGME and DiEGME, and their solutions with fuel and water, such as dissolution rate, freeze point suppression, viscosity, water solubility, and temperature dependent fuel/water partitioning. These were performed in order to determine if TriEGME is a feasible option for the replacement of DiEGME. In regards to solubility, at temperatures below -25°C, TriEGME and DiEGME exhibited similar solubility levels in fuels. Most importantly however, at -47°C TriEGME and DiEGME had equilibrium concentrations of 0.1000 ± 0.005 and 0.045 ± 0.004 vol% respectively which shows that TriEGME should be less likely to precipitate and cause fuel system fouling at very low fuel temperatures. The freeze points of DiEGME and TriEGME mixtures were also very similar up to 55 vol% saturatation. At 60 vol% concentration, the freeze points of DiEGME and TriEGME began to deviate by 15°C with DiEGME having the lower freeze point temperature. Although results were unable to be provided using the DSC from 60-100 vol %, it is suspected that either a eutectic point is reached where the freeze point may decrease and subsequently increase, or the freeze point temperature with respect to concentration continues to decrease as it approaches 100 vol% maintaining an approximate 15 degree difference between DiEGME and TriEGME.

Based on the results, DiEGME has better low temperature freeze point suppression capabilities relative to TriEGME, however 60-100 vol% concentration is never achieved in the aqueous phase. Further studies were undergone to determine if initial fuel/FSII concentration had an influence on the solubility of free water. Initial concentrations of DiEGME and TriEGME did not have an effect on the solubility levels of free water in the fuel phase, however, these studies were conducted under ambient conditions and temperature dependent analysis is recommended for fuels, especially for lower temperature observations. This study is also recommended for static partitioning analysis of DiEGME and TriEGME where under ambient conditions, both additives exhibited the similar partitioning rates from the fuel to aqueous phase. With the perceived increase in viscosity following the partitioning of FSII from the fuel to aqueous phase, studies were conducted to determine if this increase in viscosity could perhaps have an effect on the flowability of fuel. The results of this study however only showed a proportional increase in viscosity with respect to vol % concentration of FSII in the aqueous phase. The inability of the Tannas Scanning Brookfield Plus Two Viscometer to measure viscosity and record data beyond 105 cP made the observation for aqueous phase concentrations beyond 40 vol% unknown.

MDA Studies in Methanol & Fuel Matrix:

Studies were also performed, using the HPLC-MS instrument, for the characterization of MDA and copper speciation at low detection limits. These studies also provided insight into the kinetics, reaction mechanism and overall reactivity of MDA and its ability to scavenge metals in solution. Characterization of all analytes tested within a

methanol and fuel matrix were done where proton and sodium ions were attached during the electrospray ionization process. For characterization studies of MDA, Cu(II)AcAc and MDA-Cu(II) complex, a lower detection limit was observed within a methanol matrix when compared to a fuel matrix. This difference in detection limits, which is based on response of the respective analytes, has been attributed to a greater ease of ionizability within the methanol matrix when compared to the fuel matrix.

For MDA characterization, within a methanol matrix, the attached sodium ion form, gave a relative response approximately 50% greater which is perhaps due to the greater affinity of Na^+ ions than H^+ ions to be attached to the analyte during the ionization process at the electrospray source. With such high response levels at 1 µg/L (10,000+ counts), it is suspected that a lower detection limit for the protonated form of MDA within a methanol matrix can be attained. For MDA characterization with a fuel matrix, the attached sodium ion form gave a noisy response greater than that of the protonated form of MDA. For the protonated form of MDA, the detection limit of MDA was approximately 25 µg/L.

For Cu(II)AcAc characterization within a methanol matrix, the protonated and sodiated forms had a detection limit of 6,000 µg/L and 1,500 µg/L with the sodiated form having a response factor nearly sixty times that of the protonated form. With a range of 0-50 µg/L typically being found for copper in fuels, a lower detection limit for Cu(II)AcAc is desired using the HPLC-MS instrument. Within a fuel matrix, Cu(II)AcAc was unable to be characterized or calibrated successfully. Both the attached proton and sodium ion forms gave a varied relative response and as concentration increased the response factor

varied $\pm$ 1,000 counts, which has been attributed to the inability to ionize properly or fragmentation upon ionization.

100% MDA speciation within the methanol matrix was calibrated from 1-80 μg/L using the HPLC-MS instrument. Of the six isotopes characterized for the MDA-Cu(II) complex (sodiated or protonated) the isotope with m/z: 344.05805 and m/z: 366.04055 provided the highest response and the lowest respective detection limits. This case was observed within studies conducted within a fuel matrix as well, however, the efficiency of MDA to complex with copper was 70% and reaction equilibrium required a longer time compared to studies conducted within a methanol matrix.

Overall, the ability to successfully characterize, using the HPLC-MS instrument, MDA, Cu(II)AcAc and MDA-Cu(II) provides a valuable first step for fuel scientists to understand the chemistry of metal speciation in fuels. Over time, new HPLC-MS instrument methods can be developed to address deeper inquiries regarding fuel chemistry.

FUTURE WORK

A future study for analyzing the effect of initial FSII concentration on water solubility in fuel may include a more extensive temperature analysis. Varying temperature while performing these studies would provide further information on the effect of FSII on water solubility in fuel based on temperatures typically experienced within a fuel tank during storage and flight. As previously mentioned, a limitation to the work reported is that only room/ambient temperatures were studied. Suggested studies could be performed using an environmental chamber to vary the temperature above or below ambient during the exposures.

Another possibility of a modified study would be to improve sensitivity of Cu(II)AcAc within the methanol and fuel matrix. As previously discussed, derivatization techniques have demonstrated success when dealing with such compounds by silylating surface active functional groups. It is highly unlikely such a technique could work for Cu(II)AcAc, however an attempted is recommended. Another way to address the sensitivity issue of Cu(II)AcAc is to decrease the acetic acid concentration of the HPLC-MS mobile phase solution or look for fragments associated with the suspected reaction between H^+ ions and Cu(II)AcAc molecules.

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